

Density Functional Calculations of the Potential Energy Surface, Vibrational States and Infrared Spectra of CCl_3F

Diploma-thesis by
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Abstract

Density functional theory is used to generate potential energy surfaces in normal coordinates for four isotopomers of trichlorofluoromethane: $\text{C}^{35}\text{Cl}_3\text{F}$, $\text{C}^{35}\text{Cl}_2^{37}\text{ClF}$, $\text{C}^{35}\text{Cl}^{37}\text{Cl}_2\text{F}$ and $\text{C}^{37}\text{Cl}_3\text{F}$. *Ab initio* calculations using DFT of geometries suggested that the PEB0 functional is the most suitable. A new only linear scaling way to determine an anharmonic surface is presented. This approach uses energies plus gradient plus second derivatives and is tested by comparison with a surface being determined by ten times more single point potential energy calculations. The variational code MULTIMODE and the perturbation theory code SPECTRO are used to analyse the various potential energy and electric dipole moment hyper surfaces. Vibrational levels for fundamentals, overtones and combination bands are presented, as well as harmonic frequencies, anharmonic constants, rotational constants, absorption intensities and force constants for the four most abundant isotopomers of CCl_3F .

Zusammenfassung

Mit Dichtefunktionaltheorie wurde die potentielle Energiehyperfläche in Normalkoordinaten für die vier Isotopomere $\text{C}^{35}\text{Cl}_3\text{F}$, $\text{C}^{35}\text{Cl}_2^{37}\text{ClF}$, $\text{C}^{35}\text{Cl}^{37}\text{Cl}_2\text{F}$ und $\text{C}^{37}\text{Cl}_3\text{F}$ erzeugt. *Ab initio* Geometrieberechnungen mit DFT zeigten, dass das PEB0-Funktional am geeignetsten für das Ermitteln der Hyperfläche ist. Eine neue linear skalierende Methode zum Bestimmen der anharmonischen Hyperfläche wurde entwickelt. Sie berücksichtigt nicht nur den Verlauf der potentiellen Energie sondern auch den der Gradienten und der zweiten Ableitungen und zeigte gute Resultate im Vergleich mit einer 2D-Fläche. Das variationelle Programm MULTIMODE und das störungstheoretische Programm SPECTRO wurden zum Bestimmen von Fundamentalen, Obertönen und Kombinationsbanden sowie von harmonischen Frequenzen, Anharmonizitätskonstanten, Rotationskonstanten, Absorptionsintensitäten und Kraftkonstanten für die vier häufigsten Isotopomere verwendet.

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Chapter 1

Introduction

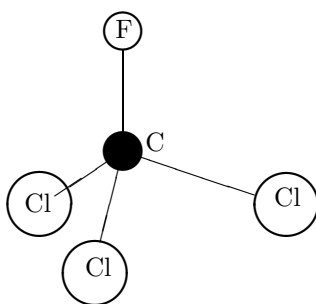
Motivation

Trichlorofluoromethane (CCl_3F , freon 11) is a very stable and nontoxic compound which has wide industrial application especially in refrigeration. It is well known for its role in the depletion of the ozonelayer which is a consequence of its stratospheric photolysis leading to the occurrence of chlorine radicals [1, 2, 3]. Furthermore, because of its strong absorption in the region of the "atmospheric window" it is such an important green house gas in the earth's atmosphere [4, 5] that it is even proposed as a "super" green house gas which might be used to "keep Mars warm" in the future [6]. Its CF-stretching mode ν_1 at 1113 cm^{-1} and the degenerate CCl-stretching vibration at 846 cm^{-1} are basically responsible for this. While the first absorption is not very specific, most fluorocarbons absorb there as well, the latter is even used for analytical measurements [7]. CCl_3F has also been a testing system [8] for IR-multiphoton excitation [9]. Finally, CCl_3F might be an interesting prototype system for the general aspects of anharmonically coupled vibrational states and intramolecular vibrational redistribution [10], [11, (b)]. For all these reasons the theory of anharmonic vibrations and IR-Spectra of CCl_3F is important.

Previous studies and the experimental point of view

Snels *et al.* [4] underlined the importance of understanding the infrared spectra of freons. They have measured and partly analysed high-resolution infrared spectra for mixtures of the isotopomers of CCl_3F . For CCl_3F there are 30 possible isotopomers for all the permutations of ^{12}C , ^{13}C , ^{14}C , ^{35}Cl , ^{36}Cl , ^{37}Cl . Therefore even a spectrum of only the most abundant species with ^{12}C and ^{35}Cl , ^{37}Cl is already difficult to analyse. Special techniques have been developed in order to tackle the increased complexity of the absorption spectrum of mixtures of isotopomers. There are three,

Figure 1.1: CCl_3F is a tetrahedral chlorofluorocarbon belonging to C_{3v} or C_s SCHÖNFLIESS symmetry group. Exact bond lengths and angles are given in table 3.1.



most commonly used techniques:

- Enrichment of one isotopomer before infrared spectroscopy experiments [5].
- Measuring a high resolution IR-spectrum for which all lines can be assigned to their isotopomers one to one. See for this references cited in [11].
- The recently developed method of Isotope Selective Overtone Spectroscopy (ISOS). This is a technically more demanding technique: a given isotopomer is rovibrationally selectively excited and then ionized by UV. The isotopomer is then identified by mass spectrometry [12].

The theoretical point of view

Highly accurate prediction of molecular vibrations has been a challenging task since ever in theoretical and physical chemistry. Quantum Chemistry allows nowadays valuable estimations of electronic potential energy hyper surfaces (PES) and - using

”theoretical spectroscopy” - the determination of all spectroscopic properties. These can be compared to already measured quantities and thus the quality of the calculations and furthermore the reliability of the out coming predictions can be judged. Many theoretical references will be quoted throughout this paper.

Subject of this thesis

The aim of this work is the calculation of the vibrational levels, intensities, fundamentals, anharmonicities and rotational constants of the isotopomers $^{12}\text{C}^{35}\text{Cl}_3\text{F}$, $^{12}\text{C}^{35}\text{Cl}_2^{37}\text{ClF}$, $^{12}\text{C}^{35}\text{Cl}^{37}\text{Cl}_2\text{F}$ and $^{12}\text{C}^{37}\text{Cl}_3\text{F}$ using Density Functional Theory (DFT). To calculate the full 9-dimensional (9D) potential energy hyper surface of this molecule one would have to span a grid of n^9 points. With n being the number of points on each vibrational degree of freedom. Usually n is greater than 10. Such a huge number of grid points is nowadays impossible to be calculated by single point calculations. Therefore the PES has to be approximated.

In this study various approximations for full dimensional potential energy surfaces are obtained. An inexpensive but sufficiently accurate approach to determine such an approximation for the potential energy surface (PES) has been developed. Coupling between up to three normal modes using energies, gradients and second derivatives, corresponding to displacements of individual normal modes is introduced. This coupling approach is used for $\text{C}^{35}\text{Cl}_3\text{F}$ only and the variational code MULTIMODE [13] is applied to this PES to calculate the vibrational levels. The perturbation theory code SPECTRO [14] is used to determine both vibrational levels and additional spectroscopic constants and intensities. The results obtained using this PES are compared against data coming from other, more expensive, PES’s. Furthermore vibrational levels, rotational constants, intensities and anharmonic constants of all the other isotopomers are determined with the help of SPECTRO.

Miani *et al.* [15] discuss the validity of DFT for the determination of molecular spectroscopic constants in comparison to coupled cluster and Møller-Plesset perturbation methods. They used SPECTRO to successfully determine the anharmonicities for the 12 atom molecule benzene. In this work SPECTRO is used for two reasons: First it provides the possibility to obtain more information about the quality of the surfaces by comparison to experiment and secondly spectroscopic constants which are experimentally difficult to observe can be determined. Thus by the means of the results of this present work the band positions and identification of vibrational transitions might become complete [14]. The MULTIMODE-code has been extensively tested by accurate calculations of rovibrational energies of many-mode molecules [13] and several applications have already proven its suitability for spectroscopy [16, 17, 18].

Chapter 2

Theoretical background

This chapter starts with a brief outline of the Density Functional Theory (DFT) by which the points on the electronic potential energy hyper surfaces were obtained. It is then described how the surfaces are used by MULTIMODE and SPECTRO in order to obtain vibrational levels, intensities, fundamentals, anharmonicities and rotational constants. If not indicated otherwise atomic units are used throughout this work.

2.1 DFT

Although it was proposed by J. C. SLATER [19] in 1951 to replace the so called exchange term in Hartree-Fock theory by a potential depending on the electron density (as it had already been introduced by DIRAC in 1930 [20]) it is only in recent years that DFT has gained more and more reputation amongst theoretical chemists. This might have been initiated by the introduction of the HOHENBERG-KOHN theorems in 1965 when the impact of DFT for theoretical chemistry became understandable for everyone. It was at that time that the famous Nobel prize winner E. Bright WILSON pointed out his understanding of DFT. He said that if one knew the exact electron density $\rho(\mathbf{r})$, then the cusps of $\rho(\mathbf{r})$ would occur at the positions of the nuclei, and a knowledge of the gradient of the density $|\nabla\rho(\mathbf{r})|$ at the nuclei would give their nuclear charges. Thus, he said, the full HAMILTONIAN would be known because it is completely defined once the position and charge of the nuclei are given. So he argued that a knowledge of the electron density was all that was necessary for a complete determination of molecular properties. The impressive number of scientific research papers using this method to predict ground state properties underlines this position.

The underlying laws, principles and consequences of using DFT are well estab-

lished [21]. Therefore only a short summary of the most important principles will be given along with a description of the most common functionals including those used in this work.

2.1.1 Basic principles of DFT

Within the BORN-OPPENHEIMER approximation the electronic energy can be expressed as a function of the electron density. Since the electron density is itself a function of space (\mathbf{r}) the energy is a function of a function and not of an argument. This is signified by calling the energy a functional and using squared brackets:

$$E[\rho] = V_{ne}[\rho] + V_{ee}[\rho] + T[\rho] \quad (2.1)$$

KOHN and SHAM [22] defined the exchange-correlation energy:

$$E_{xc}[\rho] = V_{ee}[\rho] - J_{Coul}[\rho] + T[\rho] - T_s[\rho] \quad (2.2)$$

which they reorganized to

$$V_{ee}[\rho] + T[\rho] = E_{xc}[\rho] + J_{Coul}[\rho] + T_s[\rho] \quad (2.3)$$

in order to obtain for the energy by substituting eq. (2.3) into eq. (2.1):

$$E[\rho] = V_{ne}[\rho] + E_{xc}[\rho] + J_{Coul}[\rho] + T_s[\rho] \quad (2.4)$$

Here V_{ne} stands for the nucleus-electron interaction potential

$$V_{ne}[\rho] = - \sum_i \int \frac{\rho(\mathbf{r})Z_n}{r_{ne}^{(i)}} d\mathbf{r} \quad (2.5)$$

$$= \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} \quad (2.6)$$

T_s is the kinetic energy

$$T_s[\rho] = \langle \Psi_s | \sum_i^N (-\frac{1}{2} \nabla_i^2) | \Psi_s \rangle \quad (2.7)$$

$$= \sum_i^N \langle \phi_i | -\frac{1}{2} \nabla^2 | \phi_i \rangle \quad (2.8)$$

and J_{Coul} is the Coulomb potential between two electrons i and j :

$$J_{Coul}[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_i)\rho(\mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{r}_i d\mathbf{r}_j \quad (2.9)$$

Such, within the KOHN-SHAM definition (eq. (2.4)) the difference between T and T_s as well as the non classical part of V_{ee} are represented solely by the exchange-correlation energy $E_{xc}[\rho]$. The exact form of this term is for molecular systems unknown and must be approximated. Would the exact term be known the SCHRÖDINGER equation could be solved exactly. A whole branch of DFT related research is devoted to the search of sensible approximations for the exchange correlation functional.

In the (non interacting) KOHN-SHAM reference system [22] the HAMILTONIAN is

$$\hat{\mathcal{H}}_s = - \sum_i \frac{1}{2} \nabla_i^2 + \sum_i v_s(\mathbf{r}_i) \quad (2.10)$$

where v_s is the KOHN-SHAM potential which can be derived with the help of the second HOHENBERG-KOHN theorem and via an EULER-LAGRANGE equation:

$$\begin{aligned} v_s(\mathbf{r}) &= v(\mathbf{r}) + \frac{\partial J_{Coul}[\rho]}{\partial \rho(\mathbf{r}_i)} + \frac{\partial E_{xc}[\rho]}{\partial \rho(\mathbf{r})} \\ &= v(\mathbf{r}) + j_{coul} + v_{xc}(\mathbf{r}) \end{aligned} \quad (2.11)$$

where

$$\begin{aligned} v_{xc}(\mathbf{r}) &= \frac{\partial E_{xc}[\rho]}{\partial \rho(\mathbf{r})} \\ j_{coul} &= \frac{1}{2} \int \frac{\rho(\mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{r}_j \end{aligned}$$

Here $v(\mathbf{r})$ is defined within the context of eq. (2.6).

The single Slater determinantal wavefunction Ψ_s for N' non interacting electrons in N orbitals ϕ_i is given by:

$$\Psi(\phi_1, \dots, \phi_N)_s = \frac{1}{(N!)^{1/2}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \dots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \dots & \phi_N(2) \\ \vdots & \vdots & & \vdots \\ \phi_1(N') & \phi_2(N') & \dots & \phi_N(N') \end{vmatrix} \quad (2.12)$$

The KOHN-SHAM model states that every electron is in its own non interacting orbital: $N' = N$ (obeying thus automatically PAULI's exclusion principle) and that all orbitals are part of the solution of the SCHRÖDINGER equation.

It is more convenient to use the common short-hand notation in which only the diagonal elements of the Slater determinant occur:

$$|\Psi_s\rangle = |\phi_1, \phi_2, \dots, \phi_N\rangle \quad (2.13)$$

Here ϕ_i are defined as the N lowest eigenstates of the one-electron HAMILTONIAN:

$$\hat{h}_s \phi_i = \left[-\frac{1}{2} \nabla^2 + v_s(\mathbf{r}) \right] \phi_i = \varepsilon_i \phi_i \quad (2.14)$$

The density for such a system is given by $\rho(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r})|^2$ and its integral is $\int \rho(\mathbf{r}) d\mathbf{r} = N$: the total number of electrons. As usual the solution of the SCF-procedure can be easily achieved by expanding the orbitals in terms of appropriate basis sets:

$$\phi_i = \sum_{\alpha} c_{\alpha i} \eta_{\alpha} \quad (2.15)$$

Where $c_{\alpha i}$ are the coefficients of the linear combination and η_{α} are the basis functions. Most common is the linear combination of gaussian type orbitals (GTO) in order to "simulate" slater type orbitals (STO). STO would be the best functions for molecular orbitals however the evaluation of the required integrals of GTO is much easier.

Thus - in analogy to the HARTREE-FOCK equations

$$0 = \sum_{\beta} \left\langle \eta_{\alpha} \left| -\frac{1}{2} \nabla^2 + v(\mathbf{r}) + \hat{j}_{coul} - \int \sum_i \frac{\phi_i(\mathbf{r}_k) \phi_i(\mathbf{r}_l)}{|\mathbf{r}_k - \mathbf{r}_l|} d\mathbf{r}_l P_{\mathbf{r}_k \mathbf{r}_l} - \varepsilon_i \right| \eta_{\beta} \right\rangle c_{\beta i} \quad (2.16)$$

where the permutation operator

$$P_{\mathbf{r}_k \mathbf{r}_l} \phi_i(\mathbf{r}_k) = \phi_i(\mathbf{r}_l) \quad (2.17)$$

- we can write down the KOHN-SHAM equations:

$$0 = \sum_{\beta} \left\langle \eta_{\alpha} \left| -\frac{1}{2} \nabla^2 + v(\mathbf{r}) + \hat{j}_{coul} + v_{xc}(\mathbf{r}) - \varepsilon_i \right| \eta_{\beta} \right\rangle c_{\beta i} \quad (2.18)$$

and may use a SCF-procedure.

An important and advantageous difference between eq. (2.16) and (2.18) is that the exchange-correlation potential in the latter may be expressed multiplicatively and locally since it does not depend on two electrons. Furthermore, if an exact expression for the exchange-correlation potential was found the exact electron density would be known. Unlike variational quantum chemistry methods it is impossible to systematically improve the accuracy of the exchange correlation functional. The different approximations towards the exchange-correlation functional $E_{xc}[\rho]$ are represented in the form of functionals. In the following a few common functionals are presented.

2.1.2 Functionals in DFT

In this section any spin distributions for open shell systems are not taken into account. It should be noted that all expressions are therefore only valid for closed shell systems.

LDA

The Local Density Approximation (LDA) represents a model which is deduced from an exact solution for the exchange correlation functional: the uniform electron gas. This simple approximation was introduced in 1927 [23, 24]. The exchange-correlation term splits up into two terms: the exchange functional and the correlation functional:

$$E_{xc}[\rho] = E_c[\rho] + E_x[\rho] \quad (2.19)$$

And the LDA ground state energy is thus

$$E^{LDA} = T_s + E_x^{LDA} + E_c^{LDA} \quad (2.20)$$

Here the DIRAC exchange formula [20] states that

$$\begin{aligned} E_x^{LDA}[\rho] &= -C_x \int \rho(\mathbf{r})^{4/3} d\mathbf{r} \\ C_x &= \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \end{aligned} \quad (2.21)$$

From this follows with the help of scaling relations (without demonstration):

$$E_x^{LDA}[\rho] = \int v_x(\mathbf{r})(3 + \mathbf{r} \cdot \nabla) \rho(\mathbf{r}) d\mathbf{r} \quad (2.22)$$

where

$$v_x^{LDA}(\mathbf{r}) = - \left(\frac{3}{\pi} \rho(\mathbf{r}) \right)^{1/3} \quad (2.23)$$

In 1980 CEPERLEY and ALDER simulated the ground state energy of the uniform electron gas (UEG) with the help of quantum Monte Carlo method [25]. This allowed the determination of the remaining correlation part by simple subtraction:

$$E_c[\rho] = E_{MCsimul} - T_s - E_x =: E_c^{LDA} \quad (2.24)$$

$$= \int \rho(\mathbf{r}) \varepsilon_c d\mathbf{r} \quad (2.25)$$

$$\text{where} \quad \varepsilon_c = f(r_s(\rho)) = f(\rho) \quad (2.26)$$

Here the WIGNER-SEITZ radius is explained to be $r_s(\rho) = \left(\frac{3}{4\pi\rho}\right)^{1/3}$. The determined $f(r_s)$ which fits best to the simulated results has the form:

$$\begin{aligned} \varepsilon_c(r_s) = & \frac{A}{2} \left[\ln\left[\frac{x^2}{X(x)}\right] + \frac{2b}{Q} \tan^{-1}\left[\frac{Q}{2x+b}\right] \right. \\ & \left. - \left[\ln\left[\frac{(x-y)^2}{X(x)}\right] + \frac{2(b+2y)}{Q} \tan^{-1}\left[\frac{Q}{2x+b}\right] \right] \right] \end{aligned} \quad (2.27)$$

A, Q, b, c, y are fit parameters. $x = r_s^{1/2}$ and $X(x) = x^2 + bx + c$, $X(y)$ analogously.

GGA

The Generalized Gradient Approximation(GGA) differs from LDA in that it takes into account the inhomogeneity of electron density in molecules. This is performed by introducing the gradient of electron density into the exchange functional of LDA. There are several functionals using the GGA. The most famous pure GGA exchange functional - B88 - was developed in 1988 by BECKE [26]:

$$E_x^{B88} = E_x^{LDA} - \sum_{\sigma} \int \rho_{\sigma}^{4/3} \frac{\beta x_{\sigma}^2}{1 + 6\beta x_{\sigma} \sinh^{-1}[x_{\sigma}]} d\mathbf{r} \quad (2.28)$$

Here x_{σ} introduces the gradient:

$$x_{\sigma} = \frac{|\nabla \rho_{\sigma}|}{\rho_{\sigma}^{4/3}} \quad (2.29)$$

and β is a parameter which is fitted to the HARTREE-FOCK exchange energies of six noble gas atoms.

LEE, YANG and PARR presented also in 1988 an improved, density gradient dependent correlation functional [27]. From this the following expression for a closed shell system could be derived by MIEHLICH, SAVIN, STOLL and PREUSS in 1989 [28]:

$$\begin{aligned} E_c^{LYP} = & -a \int \frac{\rho}{1 + d \cdot \rho^{-1/2}} d\mathbf{r} - \\ & ab \int \omega \rho^2 \left[C_F \rho^{8/3} + (5/12 - \frac{7}{12}\delta) |\nabla \rho|^2 - \frac{11}{24} \rho^2 |\nabla \rho|^2 \right] d\mathbf{r} \\ \text{where } \omega = & \frac{\exp[-c\rho^{-1/3}]}{1 + d\rho^{-1/3}} \rho^{-11/3} \\ C_F = & \frac{3 \cdot (3\pi^2)^{2/3}}{10} \end{aligned} \quad (2.30)$$

$$\text{and } \delta = c\rho^{-1/3} + \frac{d\rho^{-1/3}}{1 + d\rho^{-1/3}}$$

The development of LYP did not take place within the approximation of the uniform electron gas. Instead it was derived from an approximate correlation formula for helium in the context of variational wave function based theory. The fit of the parameters to the helium atom yielded

$$\begin{aligned} a &= 0.04918 \\ b &= 0.132 \\ c &= 0.2533 \\ d &= 0.349 \end{aligned}$$

Its combination with E_x^{B88} gives the well known BLYP functional. So, BLYP uses DIRAC's LDA exchange functional + BECKE's correction + LYP correlation functional.

Hybrid functionals

In 1993 BECKE introduced nonlocality by applying Adiabatic Connection Functionals [29, 30]. These functionals connect interacting and non interacting ground states as a function of a parameter λ . Here the limit $\lambda = 0$ stands for the exchange contribution of a Slater determinant while $\lambda = 1$ corresponds to the fully interacting system containing exchange and correlation energy.

$$E_{xc} = \int_0^1 \langle \Psi_n^{min,\lambda} | \hat{V}_{ee} | \Psi_n^{min,\lambda} \rangle d\lambda - J_{Coulomb}[\rho] \quad (2.31)$$

$\Psi_n^{min,\lambda}$ is the wavefunction which minimizes $\langle \Psi | \hat{T} + \lambda \cdot \hat{V}_{ee} | \Psi \rangle$ and gives the exact electron density ρ for a given λ . BECKE derived from this the so called *half-and-half* formula for the exchange correlation energy part: he approximated the λ -integration with a two-point quadrature, i.e. evaluated the integrand only twice using the exact exchange functional (HF) for $\lambda = 0$, the LDA exchange correlation functional for $\lambda = 1$, respectively:

$$E_{xc}^{half-half} = \frac{1}{2} E_x^{\lambda=0, HF} + \frac{1}{2} E_{xc}^{\lambda=1, LDA} \quad (2.32)$$

Here

$$E_x^{HF} = - \sum_{ij} \int \int \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) \frac{1}{\mathbf{r}_{12}} \phi_j(\mathbf{r}_1) \phi_i(\mathbf{r}_2) \quad (2.33)$$

Thus, in the *half-and-half* formula $E_{xc}^{half-half}$ is a linear function in λ . In order to improve the results obtained by the *half-half* formula BECKE extended the expression for the exchange correlation functional to higher order in λ . He introduced semiempirical coefficients and gradient corrected functionals:

$$E_{xc} = E_{xc}^{GGA} + c_x E_x^{HF} \quad (2.34)$$

These functionals represent a hybrid between pure density functionals for exchange correlation and exact HARTREE-FOCK exchange terms. They are referred to as DFT/HF *hybrid* functionals or as ACM (*adiabatic connection method*) functionals. A very popular hybrid functional is B3LYP.

B3LYP

The commonly used B3LYP functional is represented by:

$$\begin{aligned} E_{xc}^{B3LYP} &= A E_x^{LDA} + (1 - A) E_x^{HF} + B E_x^{B88} \\ &\quad + (1 - C) E_c^{LDA} + C E_c^{LYP} \\ A &= 0.8, B = 0.72, C = 0.81 \end{aligned} \quad (2.35)$$

Where all functionals are mentioned above and the parameters are fitted semi-empirically.

2.1.3 Functionals used in this work

B97-1

The B97-1 functional which has been used in this work is a hybrid functional which had been presented by BECKE in 1997 [43]. It is constructed starting from eq. (2.34):

$$\begin{aligned} E_{xc}^{B97-1} &= E_{xc}^{GGA} + c_x E_x^{HF} \\ &= E_x^{GGA} + E_c^{GGA} + c_x E_x^{HF} \end{aligned} \quad (2.36)$$

The *hybrid* parameter was fitted to be $c_x = 0.21$. BECKE basically approximated the GGA terms in eq. (2.36) by a polynomial fit of second order in density dependent terms:

$$E_x^{GGA} = \sum_{\sigma} \int e_{x\sigma}^{LDA}(\rho_{\sigma}) g_{x,m}(s_{\sigma}^2) d\mathbf{r} \quad (2.37)$$

here $\sigma = \alpha$ or β -spin

$g_{x,m}(s_\sigma^2)$ is the polynomial representation:

$$g_{x,m}(s_\sigma^2) = \sum_{i=0}^{m=2} c_{x\sigma,i} u_{x\sigma}^i(s_\sigma^2) \quad (2.38)$$

$$\text{where } u_{x\sigma}(s_\sigma^2) = \gamma_x s_\sigma^2 \frac{1}{1 + \gamma_x s_\sigma^2} \quad (2.39)$$

$$\text{and } s_\sigma = \frac{|\nabla \rho|}{\rho^{4/3}}$$

The coefficients $c_{x\sigma,i}$ and γ are semi-empirical parameters which were fitted to a set of 93 molecules. Within B97-1 they were found to be:

$$c_{x\sigma,0} = 0.789518 \quad c_{x\sigma,1} = 9.573805 \quad c_{x\sigma,2} = 0.660975 \\ \gamma_x = 0.004$$

The gradient corrected correlation functional in B97-1 consists of two parts

$$E_c^{GGA} = \sum_{\sigma} E_{c,\sigma\sigma} + E_{c,\alpha\beta}$$

which are described as follows:

$$E_{c,\sigma\sigma} = \int e_{c,\sigma\sigma}^{LDA}(\rho_\sigma) g_{c\sigma\sigma}(s_\sigma^2) d\mathbf{r} \quad (2.40)$$

$$\text{where } e_{c,\sigma\sigma}^{LDA}(\rho_\sigma) = e_c^{LDA}(\rho_\sigma, 0)$$

and where in analogy to the exchange part

$$g_{c,\sigma\sigma}(s_\sigma^2) = \sum_{i=0}^{m=2} c_{c,\sigma\sigma,i} u_{c,\sigma\sigma}^i(s_\sigma^2) \quad (2.41)$$

$$\text{with } u_{c,\sigma\sigma} = \gamma_{c,\sigma\sigma} s_\sigma^2 \frac{1}{1 + \gamma_{c,\sigma\sigma} s_\sigma^2}$$

The coefficients yielded from the fits are

$$c_{c\sigma\sigma,0} = 0.0820011 \quad c_{c\sigma\sigma,1} = 2.71681 \quad c_{c\sigma\sigma,2} = -2.87103 \\ \gamma_{c,\sigma\sigma} = 0.2$$

For the correlation between α and β spin electrons BECKE derived

$$E_{c,\alpha\beta} = \int e_{c,\alpha\beta}^{LDA}(\rho_\alpha, \rho_\beta) g_{c,\alpha\beta}(s_{avg}^2) d\mathbf{r} \quad (2.42) \\ e_{c,\alpha\beta}^{LDA}(\rho_\alpha, \rho_\beta) = e_c^{LDA}(\rho_\alpha, \rho_\beta) - e_x^{LDA}(\rho_\alpha, 0) - e_c^{LDA}(0, \rho_\beta)$$

$$g_{c,\alpha\beta}(s_{avg}^2) = \sum_{i=0}^m c_{c,\alpha\beta,i} u_{c,\alpha\beta}^i$$

$$\text{with } u_{c,\alpha\beta} = \gamma_{c,\alpha\beta} s_{avg}^2 \frac{1}{1 + \gamma_{c,\alpha\beta} s_{avg}^2}, \quad s_{avg}^2 = \frac{1}{2} (s_\alpha^2 + s_\beta^2)$$

The semi-empirical parameters are:

$$c_{c\alpha\beta,0} = 0.955689 \quad c_{c\alpha\beta,1} = 0.788552 \quad c_{c\alpha\beta,2} = -5.47869$$

$$\gamma_{c,\alpha\beta} = 0.006$$

PBE0

PBE0 [31, 32] is the other functional which has been used in this work. This is a one parameter hybrid functional which uses $3/4E_x^{PBE}$ and $1/4E_x^{HF}$ as the adiabatic connection thus constituting a HF/DF functional.

$$E_x^{PBE} = \int F_x^{PBE} \rho^{4/3} d\mathbf{r} \quad (2.43)$$

where

$$F_x^{PBE} = \frac{bx^2}{1 + ax^2} + 1 \quad (2.44)$$

with $b = 0.00336$, $a = 0.00449$ and $x = \frac{|\nabla\rho|}{\rho^{4/3}}$ as semi-empirical parameters.

The actual PBE0 exchange correlation combines the E_{xc}^{GGA} with E_x^{PBE} and E_x^{HF} :

$$E_{xc}^{PBE0} = E_{xc}^{PBE} + \frac{1}{4}(E_x^{HF} - E_x^{PBE}) \quad (2.45)$$

where

$$E_{xc}^{PBE} = E_x^{LDA} + E_x^{PBE} + E_c^{PBE} \quad (2.46)$$

E_x^{LDA} is defined in eq. (2.21), E_x^{PBE} is given above (eq. (2.43)) and the PBE correlation term is

$$E_c^{PBE} = \int \rho \left(\varepsilon_c^{unif}(r_s, \zeta) + H^{PBE}(r_s, \zeta, t) \right) d\mathbf{r} \quad (2.47)$$

$$H^{PBE}(r_s, \zeta, t) = \gamma \phi^3 \ln \left[1 + \frac{\beta}{\gamma} t^2 \left(\frac{1 + At^2}{1 + At^2 + At^4} \right) \right] \quad (2.48)$$

$$\text{here } \gamma = 0.031091$$

$$\text{and } \phi = \frac{1}{2} \left([1 + \zeta]^{2/3} + [1 - \zeta]^{2/3} \right)$$

$$\text{where } \zeta = \frac{\rho_\alpha - \rho_\beta}{\rho} \quad (2.49)$$

$$\begin{aligned} \text{and} \quad t &= \frac{|\nabla \rho|}{4(3/\pi)^{1/6} \phi \rho^{7/6}} \\ \text{and} \quad A &= \frac{\beta}{\gamma} \frac{1}{\left(\exp\left[\frac{-\varepsilon_c^{unif}}{\gamma \phi^3}\right] - 1 \right)} \end{aligned}$$

Eq. (2.49) becomes zero in the case of a closed shell molecule. Thus the final expression for the PBE0 functional is:

$$E_{xc}^{PBE0} = E_x^{LDA} + \frac{3}{4}E_x^{PBE} + E_c^{PBE} + \frac{1}{4}E_x^{HF} \quad (2.50)$$

2.2 Spectroscopic programs

2.2.1 MULTIMODE

$\text{C}^{35}\text{Cl}_3\text{F}$ belongs to the C_{3v} symmetry group. However, in order to deal with the problem MULTIMODE works within the C_s symmetry group. The components of the degenerate modes are treated independently. The WATSON-HAMILTONIAN [33] is used in normal coordinates. It is given in atomic units by

$$\hat{\mathcal{H}} = \frac{1}{2} \sum_{\alpha\beta}^3 (\hat{J}_\alpha - \hat{\pi}_\alpha) \mu_{\alpha\beta} (\hat{J}_\beta - \hat{\pi}_\beta) - \frac{1}{2} \sum_k^N \frac{\partial^2}{\partial Q_k^2} - \frac{1}{8} \sum_\alpha^3 \mu_{\alpha\alpha} + V(Q_1, Q_2, \dots, Q_N) \quad (2.51)$$

where

- \hat{J}_α is the component of the total angular momentum,
- $\hat{\pi}_\alpha$ is the component of the vibrational angular momentum:

$$\hat{\pi}_\alpha = - \sum_{k,l} \zeta_{k,l}^\alpha Q_k \frac{\partial}{\partial Q_l} \quad (2.52)$$

- $\mu_{\alpha\beta}$ is a component of the effective reciprocal inertia tensor and
- $V(Q_1, Q_2, \dots, Q_N)$ is the total potential electronic energy as a function of the normal modes Q_i .

In MULTIMODE, matrix elements of the difficult first term in eq. (2.51) are evaluated with at most four normal coordinates being non-zero. That means that while evaluating the first term for maximal four normal modes (e.g. Q_i, Q_j, Q_k, Q_l) all the other normal modes $Q_{1\dots h, m\dots N}$ are set to zero.

The potential energy depending on N modes may be expressed by the following hierarchical expression:

$$\begin{aligned} V(Q_1, Q_2, \dots, Q_N) = & \sum_{i=1}^N V^{(1)}(Q_i) + \sum_{i \neq j}^N V^{(2)}(Q_i, Q_j) \\ & + \sum_{i \neq j \neq k}^N V^{(3)}(Q_i, Q_j, Q_k) \\ & + \sum_{i \neq j \neq k \neq l}^N V^{(4)}(Q_i, Q_j, Q_k, Q_l) + \dots \end{aligned} \quad (2.53)$$

$\sum_{i \neq j}$ means that summation is carried out over all i and j except for $i = j$: $\sum_{i \neq j} = \sum_i \sum_j (1 - \delta_{ij})$, $\sum_{i \neq j \neq k}$ and $\sum_{i \neq j \neq k \neq l}$ are defined analogously. δ_{ij} is the Kronecker symbol.

In eq. (2.53) the number of simultaneously coupled normal modes in the potential energy hyper surface is increased with each additional term.

It was demonstrated in [34, 16] that an expansion up to $V^{(4)}$ is sufficient for many small molecules as H_2CN , N_2CS , H_2CS as well as for methane and its isotopomers. Therefore, also in the case of CCl_3F the potential energy in MULTIMODE is confined to the expansion up to $V^{(4)}$. In the following this potential energy will be denoted by $V(\mathbf{Q})$:

$$V(\mathbf{Q}) := \sum_{i=1}^N V^{(1)} + \sum_{i \neq j}^N V^{(2)} + \sum_{i \neq j \neq k}^N V^{(3)} + \sum_{i \neq j \neq k \neq l}^N V^{(4)} \quad (2.54)$$

Thus the number of grid points in MULTIMODE is proportional to n^4 . n being the number of points per normal mode (see also section 2.3.2)

MULTIMODE can carry out vibrational self consistent (VSCF) and vibrational configuration interaction (VCI) calculations. The VSCF algorithm had been implemented in 1998 by CARTER et al. [34]. It is used first to obtain appropriate polynomials in normal coordinates. The excitations of the VSCF vibrational ground state form the CI basis for the VSCF-CI calculations.

Vibrational Self-Consistent-Field

The problem of solving the vibrational wave-function can be approached by proceeding in analogy to the electronic HF SCF theory (HARTREE-FOCK and SELF-CONSISTENT-FIELD theory). This was done in 1986 by J. M. BOWMAN in reference [35]. BOWMAN first introduces a separation of the vibrational wave function for the quantum state $|n_1, n_2, \dots, n_N\rangle$ by stating:

$$\Psi_{n_1, n_2, \dots, n_N}(Q_1, Q_2, \dots, Q_N) = \prod_{i=1}^N \phi_{n_i}(Q_i) \quad (2.55)$$

where $\phi_{n_i}(Q_i)$ is only a function of the single normal coordinate Q_i (here n_i represents no longer the number of grid points but the quantum number of the vibrational state of normal mode i). These 1D functions are expanded in a primitive basis of harmonic-oscillator functions. Thus in MULTIMODE the coupling between the normal modes is introduced exclusively by the HAMILTONIAN.

The variationally best form of this product function is - in analogy to HF-theory - found by a Self-Consistent-Field procedure. There is no need for antisymmetrisation since the modal wave functions are distinguishable.

Furthermore the full HAMILTONIAN is approximated by

$$H = \sum_i^N [T_i + V(Q_i)] + T_{c,i} + V_c(Q_1, \dots, Q_N) \quad (2.56)$$

where

- $V(Q_i)$ is a 1D cut of the electric PES (i.e. $V(Q_i) = V(Q_i, Q_{j \neq i} = 0)$) and
- $V_c(Q_1, \dots, Q_N) = V(\mathbf{Q}) - \sum_i^N V(Q_i)$ the difference between the full potential and the sum of all 1D cuts constituting such the complicated simultaneous coupling of all modes.
- T_i corresponds to the second derivative $(\frac{\partial^2}{\partial Q_i^2})$ of mode i in the kinetic energy operator in eq. (2.51).
- $T_{c,i}$ stands for the Coriolis coupling operator:

$$T_{c,i} = \frac{1}{2} \sum_{\alpha\beta} \hat{\pi}_{i,\alpha} \mu_{\alpha\beta} \hat{\pi}_{i,\beta} - \frac{1}{8} \sum_{\alpha} \mu_{\alpha\alpha} \quad (2.57)$$

- $\hat{\pi}_i$ (eq. (2.52)) is the vibrational angular momentum operator, which depends on two normal coordinates linked by the Coriolis coupling constant ζ (compare eq. (2.73)).

Like in HF-theory one can now replace the term which accounts for the influence of all other modes by an averaging term which is only dependent on the considered mode. So, the actual set of VSCF eigenvalue equations consists of expressions like the following for a given normal mode i :

$$\begin{aligned} 0 = & \left[T_i + V(Q_i) + \left\langle \prod_{j=1}^N \phi_{n_j}(Q_j) \right| T_{c,i} \right. \\ & \left. + V_c(Q_1, \dots, Q_N) \right| \prod_{j=1}^N \phi_{n_j}(Q_j) \rangle_{j \neq i} - \varepsilon_i \Big] \phi_{n_i}(Q_i) \end{aligned} \quad (2.58)$$

In the matrix element

$$\left\langle \prod_{j=1}^N \phi_{n_j}(Q_j) \right| T_{c,i} + V_c(Q_1, \dots, Q_N) \left| \prod_{j=1}^N \phi_{n_j}(Q_j) \right\rangle \Big|_{j \neq i}$$

integration is carried out over all coordinates except the i^{th} one. Coupling between normal mode i and all the remaining normal modes is thus averaged and exclusively introduced by these matrix elements. They are obtained with the help of the Gauss-Hermite quadrature which is a common numerical integration method [36]. Initially a coupling potential V_c is evaluated and a zero order set of modal wave functions ϕ_i^o is chosen. Then, the eigenproblem is solved and new modal wave functions and eigenvalues are obtained. This is iterated until convergence for the eigenvalues is obtained.

After convergency, the expectation value of the VSCF state $\Psi_{n_1, n_2, \dots, n_N}$ can be evaluated:

$$\begin{aligned}
& \langle \Psi_{n_1, n_2, \dots, n_N} | H | \Psi_{n_1, n_2, \dots, n_N} \rangle = E_{n_1, \dots, n_i, \dots, n_N} \\
& = \left\langle \prod_{i=1}^N \phi_{n_i}(Q_i) \left| \sum_i [T_i + V(Q_i)] + T_{c,i} + V_c(Q_1, \dots, Q_N) \right| \prod_{i=1}^N \phi_{n_i}(Q_i) \right\rangle \\
& = \left\langle \prod_{i=1}^N \phi_{n_i}(Q_i) \left| \sum_i [T_i + V(Q_i)] \right| \prod_{i=1}^N \phi_{n_i}(Q_i) \right\rangle \\
& \quad + \left\langle \prod_{i=1}^N \phi_{n_i}(Q_i) \left| T_{c,i} + V_c(Q_1, \dots, Q_N) \right| \prod_{i=1}^N \phi_{n_i}(Q_i) \right\rangle \\
& = \sum_{i=1}^N \left[\varepsilon_i - \left\langle \prod_{i=1}^N \phi_{n_i}(Q_i) \left| T_{c,i} + V_c(Q_1, \dots, Q_N) \right| \prod_{i=1}^N \phi_{n_i}(Q_i) \right\rangle \right] \\
& \quad + \left\langle \prod_{i=1}^N \phi_{n_i}(Q_i) \left| T_{c,i} + V_c(Q_1, \dots, Q_N) \right| \prod_{i=1}^N \phi_{n_i}(Q_i) \right\rangle \\
& = \sum_{i=1}^N \varepsilon_i - (N-1) \left\langle \prod_{i=1}^N \phi_{n_i}(Q_i) \left| T_{c,i} + V_c(Q_1, \dots, Q_N) \right| \prod_{i=1}^N \phi_{n_i}(Q_i) \right\rangle
\end{aligned} \tag{2.59}$$

See also [35] for more details of the above derivations.

Virtual-CI

The solution of the eigenvalue equations (2.58) by iteration yields a complete set of virtual modal wave functions as well as the best eigenstates for the defined basis. Using this complete set of modals one can construct wavefunctions for vibrationally excited states and use them as an expansion basis for CI (configuration interaction) which converge to the exact vibrational eigenvalues and eigenfunctions of the full HAMILTONIAN. As for the electronic CI, the full CI-problem is approximated by

single, single and double, single, double and triple etc. excitations. MULTIMODE goes up to four mode excitations.

VSCF-CI

There is a more advanced technique which uses selected fundamentals and excited states optimised at the SCF level as basis in CI-calculations. This overcomes a limitation of the VSCF/VSCF-CI because it allows the mixing of energetically close lying states of same symmetry. This would have been symmetry-forbidden if the total wavefunction was simply defined as a product of the single modal wavefunctions. The disadvantage of this method is that the chosen basis is no longer orthonormal since each state has been minimized on its own. Thus, orthogonalization has to be carried out additionally what makes this method computationally more demanding.

2.2.2 SPECTRO

Most of the equations presented in this section are explained in detail in reference [37]. The expressions and approximations used by SPECTRO are elucidated in length in reference [14, (a)].

SPECTRO applies second-order perturbation theory [37] which uses a Taylor series expansion of the potential energy function up to fourth order:

$$V = \frac{1}{2} \sum_i \phi_{ii} q_i^2 + \frac{1}{6} \sum_{ijk} \phi_{ijk} q_i q_j q_k + \frac{1}{24} \sum_{ijkl} \phi_{ijkl} q_i q_j q_k q_l \quad (2.60)$$

where ϕ are the harmonic force constants while the $\phi_{ii} = \omega_i$ denote the harmonic vibrational frequencies (since this is a normal coordinate space all ϕ_i and ϕ_{ij} are equal zero by definition) and the q_i are dimensionless reduced normal coordinates being related to normal coordinates Q_i by:

$$q_i = Q_i 2\pi \sqrt{\frac{c \omega_i}{h}} \quad (2.61)$$

where c is the speed of light in vacuum and h the Planck constant. As the potential energy function described in MULTIMODE is expressed in the C_s symmetry group, also in SPECTRO all isotopomers of CCl_3F are considered as asymmetric top systems. This means that in eq. (2.60) sums are running also over the individual components of degenerate normal modes. Normally it is of advantage to exploit symmetry extensively in order to decrease the number of points on the PES being necessary to calculated and in order to impose more accuracy within the fitting

procedure of the potential energy for symmetric degenerate normal modes. Already the knowledge that the molecule belongs to C_s symmetry group reduces the number of points for the concerned normal modes by a half, for C_{3v} by two thirds and so forth. In the simple isotropic case of a $C_{\infty v}$ there would be no angle dependency and all normal coordinates $q_{i_{conc}}$ concerned by symmetry can be reduced to q^{red} via PYTHAGORAS:

$$q^{red} = \sqrt{\sum_{i_{conc}} q_{i_{conc}}^2} \quad (2.62)$$

However, in the case of C_s there is an angle dependency but rotation of $\theta = \pi$ has to yield the same q . One can thus write:

$$q^{red} = \sqrt{q_{1_{conc}}^2 + q_{2_{conc}}^2} \cdot \cos[2 \cdot \theta] \quad (2.63)$$

where θ is the angle between two concerned normal modes: $\theta = \arctan[q_1/q_2]$. For CCl_3F there is C_{3v} symmetry which means that the results for rotations of $\theta = \frac{4\pi}{3}$ have to be invariant. Thus:

$$q^{red} = \sqrt{q_{1_{conc}}^2 + q_{2_{conc}}^2 + q_{3_{conc}}^2} \cdot \cos\left[\frac{3\theta}{2}\right] \quad (2.64)$$

If the last expression is incorporated into eq. (2.60) symmetry is automatically imposed within the fitting procedure generating the ϕ and the number of variables is minimised meaning that there are less points to calculate. This means that if only C_s symmetry is used for a C_{3v} symmetric molecule one does not only have to calculate more points but also to "tell" the fitting procedure which generates the ϕ that some of the fitted points are symmetrically equivalent. Otherwise the fitting procedure will break the symmetry of the forcefield and annihilate degeneracy.

The vibrational energy levels can be given by an expansion up to second order ([37]):

$$E(n_1, \dots, n_N)^{asym} = \sum_s \omega_s \left(n_s + \frac{1}{2}\right) + \sum_{s \leq s'} x_{ss'}^{asym} \left(n_s + \frac{1}{2}\right) \left(n_{s'} + \frac{1}{2}\right) + \dots \quad (2.65)$$

ω are the harmonic frequencies explained above and $x_{ss'}$ are the anharmonic constants which will be defined in the following. A complete expansion would automatically account for all symmetries. If the expansion is only used to a certain order a symmetry adopted expression would be theoretically more appropriate. This problem is treated in more detail later on in this chapter.

Fundamentals, anharmonic constants, rotational constants and transition intensities within SPECTRO

The fundamental frequency ν_i corresponding to a given normal mode i is

$$\nu_i = \omega_i + 2x_{ii} + \frac{1}{2} \sum_{k \neq i} x_{ki} \quad (2.66)$$

its overtone is:

$$n \nu_i = n(\nu_i) + n x_{ii} \quad (2.67)$$

where the (ν_i) means the value for the fundamental ν_i . The combination is:

$$(\nu_i + \nu_j) = (\nu_i) + (\nu_j) + x_{ii} + x_{jj} + x_{ij} \quad (2.68)$$

and anharmonicities are given by [?]:

$$x_{ss} = \frac{1}{16} \phi_{ssss} - \frac{1}{16} \sum_{s'} (\phi_{sss'})^2 \left(\frac{8\omega_s^2 - 3\omega_{s'}^2}{\omega_{s'}(4\omega_s^2 - \omega_{s'}^2)} \right) \quad (2.69)$$

$$\begin{aligned} x_{ss'} &= \frac{1}{4} \phi_{ss's's'} - \sum_{s''} \frac{\phi_{ss's''} \phi_{s's's''}}{4\omega_{s''}} - \sum_{s''} \frac{(\phi_{ss's''})^2 \omega_{s''} (\omega_s^2 + \omega_{s'}^2 - \omega_{s''}^2)}{2\Omega_{ss's''}} \\ &+ \sum_{\beta} B_{eq}^{\beta} [\zeta_{ss'}^{\beta}]^2 \left[\frac{\omega_s}{\omega_{s'}} + \frac{\omega_{s'}}{\omega_s} \right] \end{aligned} \quad (2.70)$$

where

$$\Omega_{ss's''} = (\omega_s + \omega_{s'} + \omega_{s''})(-\omega_s + \omega_{s'} + \omega_{s''})(\omega_s - \omega_{s'} + \omega_{s''})(\omega_s + \omega_{s'} - \omega_{s''}) \quad (2.71)$$

and B_{eq}^{β} are the equilibrium rotational constants for β : one of the principal inertia axes.

The rotational constants are proportional to the reciprocal moments of inertia, given by

$$B_{eq}^{\beta} = \frac{\hbar}{4\pi c I_{eq}^{\beta}} \quad (2.72)$$

The Coriolis constants ζ are defined by the l-matrix elements (see section 2.3.1 and 3.4):

$$\zeta_{ij}^x = \sum_i l_{yi}^j l_{zi}^k - l_{zi}^j l_{yi}^k \quad (2.73)$$

i, j and k denote normal modes. Furthermore rotational constants depend on the degree of vibrational excitations. This can be approximated by:

$$B_n^{\beta} = B_{eq}^{\beta} - \sum_i \alpha_i^{\beta} (n_k + \frac{1}{2}) \quad (2.74)$$

Here the α constant is a function of the coriolis constant, of the harmonics and - as B_{eq}^β is - of the moment of inertia I_β : $\alpha_i^\beta = f(\omega_i, \zeta_i, I_\beta)$. The explicit expression can be found in reference [37].

Amongst the quartic terms in eq. (2.70), only the diagonal ϕ_{iiii} and semi-diagonal ϕ_{iijj} terms are required to determine the vibrational levels. It is possible to calculate the quartic and cubic terms by analytic evaluation of the second derivatives at various geometries. The latter are obtained by finite displacement δq from equilibrium geometry.

$$\phi_{ijk} = \frac{\phi_{jk}(+\delta q_i) - \phi_{jk}(-\delta q_i)}{|2\delta q_i|} \quad (2.75)$$

$$\phi_{iijj} = \frac{\phi_{jj}(+\delta q_i) + \phi_{jj}(-\delta q_i) - 2\phi_{jj}(\delta q_i = 0)}{|\delta q_i|^2} \quad (2.76)$$

For each normal mode a step δq corresponding to maximal 0.008 Bohr is used. This seems to be sufficiently small and had been tested by convergence for NH_3^+ in [18].

The anharmonic corrections which lead to the electric dipole intensities are explained in detail by HANDY *et al.* [14] (b). The electric dipole moment surface pertaining to the potential energy function in eq. (2.60) expanded up to cubic terms is:

$$\begin{aligned} \mu^\alpha &= \mu_{eq}^\alpha + \sum_i \mu_i^\alpha q_i + \frac{1}{2} \sum_{i \leq j} \mu_{ij}^\alpha q_i q_j \\ &+ \frac{1}{6} \sum_{i \leq j \leq k} \mu_{ijk}^\alpha q_i q_j q_k \end{aligned} \quad (2.77)$$

where α stands for the spatial orientation of the dipole (x, y, z) , μ_{eq}^α denotes the static electric dipole moment and μ_i^α the electric dipole moment of normal mode i . The transition dipole moment for a one-quantum vibrational transition is expressed as

$$\begin{aligned} \langle n_i, n_j, \dots | \mu^\alpha | n_i + 1, n_j, \dots \rangle &= \sqrt{n_i + 1} (\mu_{i01}^\alpha + M_i^\alpha n_i + \sum_{j \neq i} M_j^\alpha n_j) \\ \text{where} \\ \mu_{i01}^\alpha &= \langle 0, 0, \dots | \mu^\alpha | n_i = 1, 0, \dots \rangle \end{aligned} \quad (2.78)$$

μ_{i01}^α represents the transition dipole moment of the fundamental i including the anharmonic corrections. Due to the assumptions of perturbation theory M_i^α and M_j^α are much smaller. They influence only the intensities of the hot-band and stimulated emission transitions which are much less intense than the fundamental.

Neglecting all M_i^α leads to the practical expression for the measured integrated absorbance of a fundamental band:

$$\begin{aligned}\mathcal{A}_i &= \mathcal{A}(\nu_i) \\ &= \sum_{n_i n_j \dots} \mathcal{A}_{n_i, n_j \dots}^{n_i+1, n_j \dots}\end{aligned}\quad (2.79)$$

$$= \frac{8\pi^3 N_A g_i \nu_i \mu_{i01}^2}{(4\pi\epsilon_0)3hc} \quad (2.80)$$

$$= \left[2.507 \frac{\text{km}}{(\text{mol cm}^{-1} \text{D}^2)} \right] g_i \nu_i \mu_{i01}^2 \quad (2.81)$$

where g_i is the degeneracy of normal mode i and

$$\mu_{i01}^2 = \sum_{\alpha=x,y,z} |\mu_{i01}^\alpha|^2 \quad (2.82)$$

The integrated band strength may be expressed in several units:

$$\mathcal{G}_i = \int_{\text{band}} \frac{\sigma(\nu)}{\nu} d\nu \quad (2.83)$$

$$= \frac{8\pi^3 g_i \mu_{i01}^2}{(4\pi\epsilon_0)3hc} \quad (2.84)$$

$$= \frac{\mathcal{A}_i}{\nu_i N_A} \quad (2.85)$$

$$\mathcal{G}_i \simeq 16.6054 \frac{\mathcal{A}_i / \frac{\text{km}}{\text{mol}}}{\nu_i / \text{cm}^{-1}} \text{pm}^2 \quad (2.86)$$

However, this expression does not take into account the BOLTZMANN weighted population for the lowest vibrational states. This may be problematic in the case of low lying fundamentals and high temperatures. Then the measured integrated band strength includes hot band transition while \mathcal{G}_i in eq. (2.86) accounts exclusively for the fundamentals. Therefore the above expressions are correct only for transitions at 0K. For temperatures higher than 0K one has to introduce a correction by a BOLTZMANN factor:

$$\mathcal{G}_i^{\text{eff}} = \mathcal{G}_i \left[1 - g_i \exp \left[-\beta h c \nu_i \right] \right], \quad \beta = \frac{1}{kT} \quad (2.87)$$

Asymmetric and Symmetric Top HAMILTONIAN

The diagonal elements of the actually effective HAMILTONIAN in the harmonic oscillator representation yield for the vibrational energies of symmetric top species such

as the C_{3v} symmetric molecules $C^{35}Cl_3F$ or $C^{37}Cl_3F$ according to [37]:

$$\begin{aligned}
 E(n, l)^{sym} = & \sum_s \omega_s(n_s + \frac{1}{2}) + \sum_{s \geq s'} x_{ss'}^{sym}(n_s + \frac{1}{2})(n_{s'} + \frac{1}{2}) \\
 & + \sum_t \omega_t(n_t + 1) + \sum_{t \geq t'} x_{tt'}^{sym}(n_t + 1)(n_{t'} + 1) \\
 & + \frac{1}{2} \sum_{s, t} x_{st}^{sym}(n_s + \frac{1}{2})(n_t + 1) + \sum_{t \geq t'} g_{tt'} l_t l_{t'} \quad (2.88)
 \end{aligned}$$

constituting such an expression which takes into account the degeneracy and its interactions:

- s is standing for a non-degenerate normal mode
- t for a degenerate normal mode
- while n and l are the quantum numbers associated with vibration and vibrational angular momentum, respectively.

While going from eq. (2.65) to (2.88) an increase in symmetry should not affect the correct description i.e. the same eigenvalue spectrum is obtained for both expressions. But if one is interested in the anharmonic constants of the more compact expression (2.88) the most straight forward would be to use the symmetric top HAMILTONIAN. In this case one would have to express the x^{sym} and g as functions of the force constants. In principle the force field is independent of the choice of the HAMILTONIAN since the PES of any molecule does not depend on the observer's picture of the molecule's symmetry. However the fitting procedure which leads to the effective HAMILTONIAN should respect symmetry. According to [37] the following relations link the force field with the vibrational spectrum: For the non degenerate modes s .

$$x_{ss} = \frac{1}{16} \phi_{ssss} - \frac{1}{16} \sum_{s'} (\phi_{sss'})^2 \left[\frac{8\omega_s^2 - 3\omega_{s'}^2}{\omega_{s'}(4\omega_s^2 - \omega_{s'}^2)} \right] \quad (2.89)$$

$$\begin{aligned}
 x_{ss'} = & \frac{1}{4} \phi_{ss's'} - \sum_{s''} \frac{\phi_{sss''} \phi_{s's's''}}{4\omega_{s''}} - \sum_{s''} \frac{(\phi_{ss's''})^2 \omega_{s''} (\omega_s^2 + \omega_{s'}^2 - \omega_{s''}^2)}{2\Omega_{ss's''}} \\
 & + B_e^{(z)} (\zeta_{ss'}^{(z)})^2 \left[\frac{\omega_s}{\omega_{s'}} + \frac{\omega_{s'}}{\omega_s} \right] \quad (2.90)
 \end{aligned}$$

For the non degenerate/degenerate interactions st :

$$x_{st} = \frac{1}{4} \phi_{sst_a t_a} - \frac{1}{4} \sum_{s'} \left[\frac{\phi_{sss'}^2 \phi_{t_a t_a s'}}{\omega_{s'}} \right] - \frac{1}{2} \sum_{t'} \left[\frac{\phi_{st_a t_a'}^2 \omega_{t'} (\omega_s^2 + \omega_{t'}^2 - \omega_{t'}^2)}{\Omega_{stt'}} \right]$$

$$+B_x \left[(\zeta_{sta}^{(x)})^2 + (\zeta_{sta}^{(y)})^2 \right] \left[\frac{\omega_s}{\omega_t} + \frac{\omega_t}{\omega_s} \right] \quad (2.91)$$

The diagonal anharmonic constants between degenerate modes t are:

$$\begin{aligned} x_{tt} = & \frac{1}{16} \phi_{t_a t_a t_a t_a} - \frac{1}{16} \sum_s \left[\frac{\phi_{sta}^2 (8\omega_t^2 - 3\omega_s^2)}{\omega_s (4\omega_t^2 - \omega_s^2)} \right] \\ & - \frac{1}{16} \sum_{t'} \left[\frac{\phi_{t_a t_a t'_a}^2 (8\omega_t^2 - 3\omega_{t'}^2)}{\omega_{t'} (4\omega_t^2 - \omega_{t'}^2)} \right] \end{aligned} \quad (2.92)$$

and

$$\begin{aligned} g_{tt} = & -\frac{1}{48} \phi_{t_a t_a t_a t_a} - \frac{1}{16} \sum_s \left[\frac{\phi_{sta}^2 \omega_s}{4\omega_t^2 - \omega_s^2} \right] \\ & + \frac{1}{16} \sum_{t'} \left[\frac{\phi_{t_a t_a t'_a}^2 (8\omega_t^2 - \omega_{t'}^2)}{\omega_{t'} (4\omega_t^2 - \omega_{t'}^2)} \right] + B_z (\zeta_{t_a t_b}^{(z)})^2 \end{aligned} \quad (2.93)$$

The off diagonal elements of the symmetric top anharmonic constants matrix are:

$$\begin{aligned} x_{tt'} = & \frac{1}{8} (\phi_{t_a t_a t'_a t'_a} + \phi_{t_a t_a t'_a t'_b}) - \frac{1}{4} \sum_s \left[\frac{\phi_{sta}^2 \phi_{st'_a}^2}{\omega_s} \right] \\ & - \frac{1}{4} \sum_s \left[\frac{\phi_{sta}^2 \omega_s (\omega_t^2 + \omega_{t'}^2 - \omega_s^2)}{\Omega_{stt'}} \right] - \frac{1}{2} \sum_{t''} \left[\frac{\phi_{t_a t'_a t''_a}^2 \omega_{t''} (\omega_t^2 + \omega_{t'}^2 - \omega_{t''}^2)}{\Omega_{tt't''}} \right] \\ & + \left[\frac{1}{2} B_z (\zeta_{t_a t'_b}^{(z)})^2 + B_x (\zeta_{t_a t'_a}^{(y)})^2 \right] \left[\frac{\omega_t}{\omega_{t'}} + \frac{\omega_{t'}}{\omega_t} \right] \end{aligned} \quad (2.94)$$

and

$$\begin{aligned} g_{tt'} = & -\frac{1}{2} \sum_s \left[\frac{\phi_{sta}^2 \omega_s \omega_t \omega_{t'}}{\Omega_{stt'}} \right] + \sum_{t''} \left[\frac{\phi_{t_a t'_a t''_a}^2 \omega_t \omega_{t'} \omega_{t''}}{\Omega_{tt't''}} \right] - 2B_x (\zeta_{t_a t'_a}^{(y)})^2 \\ & + B_z (\zeta_{t_a t'_b}^{(z)})^2 + 2B_z \zeta_{t_a t_b}^{(z)} \zeta_{t'_a t'_b}^{(z)} \end{aligned} \quad (2.95)$$

Thus, all anharmonic constants within the asymmetric and the symmetric top representation are accessible if the force field of the symmetric top is known. Unfortunately, in SPECTRO the routines for symmetric tops having more than one degenerate mode do not work. To correct these is not trivial and would be beyond the scope of this study.

An alternative way would be to reduce the number of parameters by transforming all $x_{ss'}^{asym}$ into their corresponding $x_{ss'}^{sym}$, x_{st}^{sym} , $x_{tt'}^{sym}$ and $g_{tt'}$. In reference [50] this has been done for benzene (belonging to the D_{6h} symmetry group). In order to check

if these transformations are equally legitimate for the case of our C_{3v} molecule one might think of a method which is straight forward: There is the condition that expression (2.65) and (2.88) have to yield the same transitional energy for a given excitation. This is easily obtained by subtracting the zeropoint energies E_0 from the corresponding descriptions and setting them equal.

Formally one can rewrite eq. (2.65) or (2.88) by vector multiplication uniting all quantum numbers in one vector (\vec{n}) and all harmonic frequencies and anharmonic constants in another one (\vec{c}):

$$E^{asym} = \vec{n}^{asym^T} \vec{c}^{asym}$$

where

$$\vec{c}^{asym} = \begin{pmatrix} \omega_1 \\ \vdots \\ \omega_N \\ x_{11} \\ \vdots \\ x_{1N} \\ x_{22} \\ \vdots \\ x_{2N} \\ \vdots \\ x_{NN} \end{pmatrix} \quad \text{and} \quad \vec{n}^{asym} = \begin{pmatrix} n_1 + 1/2 \\ \vdots \\ n_N + 1/2 \\ (n_1 + 1/2) * (n_1 + 1/2) \\ (n_1 + 1/2) * (n_2 + 1/2) \\ \vdots \\ (n_1 + 1/2) * (n_N + 1/2) \\ (n_2 + 1/2) * (n_2 + 1/2) \\ \vdots \\ (n_N + 1/2) * (n_N + 1/2) \end{pmatrix}$$

in the case of the asymmetric top description. If the zeropoint energy had already been accounted for and the analogous had been done for the symmetric top description we could write:

$$\begin{aligned} 0 &= (E^{asym} - E_0^{asym}) - (E^{sym} - E_0^{asym}) = \vec{n}^{asym^T} \vec{c}^{asym} - \vec{n}^{sym^T} \vec{c}^{sym} \\ &= (\vec{n}^{asym^T}, \vec{n}^{sym^T}) \begin{pmatrix} \vec{c}^{asym} \\ -\vec{c}^{sym} \end{pmatrix} \end{aligned} \quad (2.96)$$

This equation has to be valid for all physically possible combinations of quantum numbers within the two descriptions. The quantum number vector in eq. (2.96) can thus be enlarged to become a $m \times m$ matrix where m is the number of elements in \vec{c} . One obtains:

$$\begin{bmatrix} \vec{n}^{asym^T} & \vec{n}^{sym^T} \\ \vdots & \vdots \end{bmatrix} \begin{pmatrix} \vec{c}^{asym} \\ -\vec{c}^{sym} \end{pmatrix} = \vec{0} \quad (2.97)$$

where $[\vec{\mathbf{n}}^{\text{asym}}, \vec{\mathbf{n}}^{\text{sym}}]$ denotes the quantum number matrix.

As mentioned above, to compare the same vibrational excitations involving degenerate modes t it is crucial that the rows in the quantum number matrix consist of physically possible combinations. Meaning that not only the selection rules (l going from $-n$ to n in integer steps of 2) have to be respected but also that a given combination of quanta in the asymmetric top picture has to be combined with the *right* combination of quanta in the symmetric top picture. One could think of directly correlating the combinations following an evident scheme:

n_t^{sym}	l_t		n_{ta}	n_{tb}
1	1		1	0
"	-1		0	1
2	2		2	0
"	0		1	1
"	-2	\leftrightarrow	0	2
3	3		3	0
"	1		2	1
"	-1		1	2
"	-3		0	3
\vdots	\vdots		\vdots	\vdots

Where a and b denote the two components of a given degenerate mode. However, this would be a too simplistic correlation since it does not account for symmetry. Considering for example $n_t^{\text{sym}} = 2$ one would expect A_1 for $l = 0$ and E for $l = 2$ and -2 as irreducible representations within the C_{3v} symmetric representation. E correlates to a combination of A' and A'' in the C_s group. Thus, by assigning A' and A'' to n_{ta} or n_{tb} , respectively, one finds two A' and one A'' representations which have to be correlated. It is not evident which of the A' representations stays alone and which one joins the E representation:

Γ^{irr}	n_t^{sym}	l_t		Γ^{irr}	n_{ta}	n_{tb}
E	2	2		A''	1	1
E	2	-2	\leftrightarrow	A'	2	0
A_1	2	0		A'	0	2

The following equations have been used (from symmetry group theory):

$$\begin{aligned}
 A'' \times A'' &= A' \\
 A' \times A' &= A' \\
 A'' \times A' &= A' \times A'' = A''
 \end{aligned}$$

Thus, only one combination of quanta can clearly be assigned in the case of $n_t^{sym} = 2$: $n_{ta} = n_{tb} = 1$ (A'') and E have to be strictly degenerate, meaning that it is not clear if l is positive or negative.

Expression (2.97) is a typical set of linearly independent and dependent equations. According to a given correlation one is free to choose the quantum number elements of the matrix in this expression. The components of \vec{c}^{sym} which are unknown can thus be easily obtained by successive substitution (see chapter 3.5 and Appendix A).

2.3 The Coupling Approach

In this approach the form of the potential energy surface is restricted to an expression which takes into account coupling between up to three normal modes:

$$V(\mathbf{Q}) := \sum_{i=1}^N V^{(1)}(Q_i) + \sum_{i \neq j}^N V^{(2)}(Q_i, Q_j) + \sum_{i \neq j \neq k}^N V^{(3)}(Q_i, Q_j, Q_k) \quad (2.98)$$

where N is the total number of normal modes. The notations $\sum_{i \neq j}$ etc. have already been introduced in chapter 2.2.

2.3.1 Fitting the Derivatives

Polynomial series expansions can be used to calculate potential energies and their first and second derivatives, at discrete points on the normal modes. Specifically the representation is:

$$\sum_{i=1}^9 V^{(1)}(Q_i) \approx \sum_{i=1}^9 f_i(Q_i) \quad (2.99)$$

$$\sum_{i \neq j}^9 V^{(2)}(Q_i, Q_j) \approx \sum_{i \neq j}^9 \left(Q_i f_{ij}(Q_j) + Q_i^2 f_{iij}(Q_j) \right) \quad (2.100)$$

$$\sum_{i \neq j \neq k}^9 V^{(3)}(Q_i, Q_j, Q_k) \approx \sum_{i \neq j \neq k}^9 Q_i Q_j f_{ijk}(Q_k) \quad (2.101)$$

The fourth and higher order terms are all set to zero.

Here $f_i(Q_i)$ is a series expansion up to order 15 which is fitted to 16 potential energy points $E(Q_i)$ calculated for 16 different values of Q_i while all other $Q_{j \neq i} = 0$.

$$f_i(Q_i) := \sum_{n=0}^{15} a_{n,i} Q_i^n \quad (2.102)$$

$f_{ij}(Q_j)$ is analogously defined as a series expansion up to order 15 fitted to 16 energy gradients calculated at the same values on Q_i as the energies, evaluated at all other normal modes $Q_{i \neq j} = 0$: $\left. \frac{\partial E(Q_j)}{\partial Q_i} \right|_{Q_j; Q_i=0}$

$$f_{ij}(Q_j) := \sum_{n=0}^{15} b_{n,ij} Q_j^n \quad (2.103)$$

$f_{ijk}(Q_k)$ is a series expansion up to order 15 being fitted to 16 second derivatives on Q_i , evaluated at all other points $Q_{i \neq k} = Q_{j \neq k} = 0$: $\left. \frac{\partial^2 E(Q_k)}{\partial Q_i \partial Q_j} \right|_{Q_k; Q_i=Q_j=0}$

$$f_{ijk}(Q_k) := \sum_{n=0}^{15} c_{n,ijk} Q_k^n \quad (2.104)$$

In equation (2.99) and (2.100) the terms $b_{0,ii}$ of f_{ij} are constant and removed before insertion into the potential energy. For a deduction of this see below.

Gradients and second derivatives of the energy with respect to normal coordinates are obtained from gradients and second derivatives with respect to cartesian coordinates using the l -matrix. Since the derivatives are given by CADPAC only in cartesian coordinates transformations of each normal mode and for every nucleus have to be carried out with the help of the l -matrix. The displacement for the normal mode i and nucleus α in the cartesian coordinate x is:

$$x_{i,\alpha} - x_{i,\alpha}^{(0)} = \frac{l_{i,\alpha}^{(x)} Q_i}{m_\alpha^{1/2}} \quad (2.105)$$

where $x^{(0)}$ corresponds to the equilibrium position.

The first and the second derivatives with respect to certain normal modes j and k can be expressed as follows

$$\begin{aligned} \frac{\partial V(Q_i)}{\partial Q_j} &= \sum_{\alpha} \frac{\partial V(Q_i)}{\partial x_{j,\alpha}} \frac{\partial x_{j,\alpha}}{\partial Q_j} \\ &= \sum_{\alpha} \frac{\partial V(Q_i)}{\partial x_{j,\alpha}} \frac{l_{j,\alpha}^{(x)}}{m_\alpha^{1/2}} \end{aligned} \quad (2.106)$$

$$\frac{\partial^2 V(Q_i)}{\partial Q_j \partial Q_k} = \sum_{\alpha} \sum_{\beta} \frac{\partial^2 V(Q_i)}{\partial x_{j,\alpha} \partial x_{k,\beta}} \frac{l_{j,\alpha}^{(x)}}{m_\alpha^{1/2}} \quad (2.107)$$

$$= \sum_{\alpha} \sum_{\beta} \frac{\partial^2 V(Q_i)}{\partial x_{j,\alpha} \partial x_{k,\beta}} \frac{l_{k,\beta}^{(x)}}{m_\beta^{1/2}} \frac{l_{j,\alpha}^{(x)}}{m_\alpha^{1/2}} \quad (2.108)$$

For y and z analogously.

The potential energy surface determined as described in this section is called 'A'. It is only generated for the isotopomer $C^{35}Cl_3F$ and not for the other isotopomers

because of the computational costs (see also the beginning of 'Computational details'). It approximates the expansion for the potential energy (eq. (2.51)) only up to $V^{(3)}$.

Deduction of the Coupling Approach potential

A 3D PES would be, according to eq. (2.53) and eq. (2.99-2.104):

$$\begin{aligned}
 V(Q_i, Q_j, Q_k) = & \left[\sum_n a_{n,i} Q_i^n + \sum_n a_{n,j} Q_j^n + \sum_n a_{n,k} Q_k^n \right] \\
 & + \left[Q_i \sum_n b_{n,ji} Q_j^n + Q_i \sum_n b_{n,ki} Q_k^n + Q_j \sum_n b_{n,ij} Q_i^n \right. \\
 & \left. + Q_i \sum_n b_{n,ii} Q_i^n + Q_j \sum_n b_{n,jj} Q_j^n + Q_k \sum_n b_{n,kk} Q_k^n \right] \\
 & + \left[Q_i Q_j \sum_n c_{n,kij} Q_k^n + Q_k Q_i \sum_n c_{n,jki} Q_j^n + Q_j Q_k \sum_n c_{n,ijk} Q_i^n \right] \\
 & + \left[Q_i^2 \sum_n c_{n,jii} Q_j^n + Q_i^2 \sum_n c_{n,kii} Q_k^n + Q_j^2 \sum_n c_{n,ijj} Q_i^n \right. \\
 & \left. + Q_j^2 \sum_n c_{n,kjj} Q_k^n + Q_k^2 \sum_n c_{n,ikk} Q_i^n + Q_k^2 \sum_n c_{n,jkk} Q_j^n \right] \\
 & + \left[Q_i^2 \sum_n c_{n,iii} Q_i^n + Q_j^2 \sum_n c_{n,jjj} Q_j^n + Q_k^2 \sum_n c_{n,kkk} Q_k^n \right]
 \end{aligned} \tag{2.109}$$

Here, the first bracket would correspond to eq. (2.99), the first three terms of the second and the fourth bracket would correspond to eq. (2.100), the third bracket would correspond to eq.(2.101). The last three terms of the second bracket and the fifth bracket are redundant because they do not contain information which is not already included in the first bracket. It is reminded of the fact that the coefficients $b_{nik} \neq b_{nij}$ but that $c_{njk i} = c_{n j i k} \forall i \neq k$ (SCHWARTZ' RULE). Generalizing expression (2.109) leads to the potential energy hyper surface used within the Coupling Approach for any system with N vibrational degrees of freedom:

$$\begin{aligned}
 V(Q_1, \dots, Q_N) = & \sum_{i=1}^N \sum_n a_{n,i} Q_i^n + \sum_{i=1}^N Q_i \sum_{j \geq i} \sum_n b_{n,ji} Q_j^n
 \end{aligned}$$

$$+ \sum_{i=1}^N Q_i \sum_{j \geq i} Q_j \sum_{k \geq j} \sum_n c_{n,ijk} Q_k^n \quad (2.110)$$

The coefficients of the series expansions are obtained by a fitting procedure which is explained in chapter 2.3.1 'Fitting the Derivatives'. The PES is thus approximated by an expression which reminds of a TAYLOR expansion:

$$\begin{aligned} V(Q_1, \dots, Q_N) = & \sum_i V(Q_i, Q_{j \neq i} = 0) + \sum_i Q_i \sum_{j \geq i} \partial_{Q_i} V(Q_j, Q_{i \neq j} = 0) \\ & + \sum_i Q_i \sum_{j \geq i} Q_j \sum_{k \geq j \geq k} \partial_{Q_i Q_j}^2 V(Q_k, Q_{i \neq k} = Q_{j \neq k} = 0) \end{aligned} \quad (2.111)$$

which we express according to (2.102)-(2.104):

$$\begin{aligned} V(Q_1, \dots, Q_N) = & \sum_i f_i(Q_i) + \sum_i Q_i \sum_{j \geq i} f_{ij}(Q_j) \\ & + \sum_i Q_i \sum_{j \geq i} Q_j \sum_{k \geq j \geq k} f_{ijk}(Q_k) \end{aligned} \quad (2.112)$$

In the above expressions there are some coefficients in the series expansion which have to be equal to zero. They appear to be the constant terms of the derivative of expression (2.110) with respect to Q_i at $Q_i = 0$:

$$\begin{aligned} \left. \frac{\partial V(Q_1, \dots, Q_N)}{\partial Q_i} \right|_{Q_i=0} = & a_{1,i} \\ & + \sum_{j \neq i} \sum_n b_{n,ji} Q_j^n + \sum_{j \neq i} Q_j b_{1,ij} \\ & + b_{0,ii} \\ & + \sum_{j \neq i} Q_j \sum_{k \neq i} \sum_n c_{n,kij} Q_k^n + \sum_j \sum_{k \neq j \neq i} Q_i Q_j c_{1,ijk} \\ & + \sum_j Q_j^2 c_{1,ijj} \end{aligned} \quad (2.113)$$

2.3.2 Scaling of the Calculation Time

Supposing that for each normal mode of a given molecule with N atoms, n points have to be calculated *ab initio*, then a fully coupled potential energy hyper surface

would be represented by a grid of n^{3N-6} points. Since a full 5D PES ($\sim 100\,000$ single point calculations) is nowadays computationally still too expensive approximations are necessary for $N > 4$. The restricted form for the potential energy of eq. (2.53) scales with $(3N - 6) * n^4$. The approximation for the potential energy which we propose by combining eq. (2.53) with eq. (2.99) - (2.101) scales only with $(3N-6)*n$. However, it must be kept in mind that the Coupling Approach represents only a smooth extrapolation towards the full PES.

Chapter 3

Computational details

In this chapter is given all information which has been essential in order to obtain the results for the vibrational levels, IR absorption intensities, rotational constants and anharmonic constants but which is not directly linked to them. Results for geometries and harmonic wavenumbers for several functionals are already presented and discussed in section 3.3.

In CCl_3F there are nine vibrational degrees of freedom. Normal coordinates are used in the calculations. However, if the symmetric top isotopomers are treated there are three degenerated normal modes. This in principle reduces the number of points needed to be calculated. See for this also section 4.2.2. Besides it is more comfortable to treat the symmetric top $\text{C}^{35}\text{Cl}_3\text{F}$ since its potential energy hyper surface is more symmetric and constitutes where appropriate a kind of 'internal reference' (see section 4.4.2).

3.1 The Machines

Machines of the ETH Zürich and of Cambridge University could be used for the heavy calculations which needed to be carried out. In the ETH

- DEC 8400 6/525, 2 GB memory, 51 GB disk (6 processors)
- DEC 8400 5/300, 4 GB memory, 51 GB disk (8 processors)

(both by COMPAQ)
while in Cambridge

- SGI origin 2000, (8 processors)

were used.

3.2 The Basis Sets

The CADPAC package [38] was used throughout and TZ2P (triple zeta double polarisation) and DZP (double zeta polarisation) basis sets [39, 40]. The TZ2P basis set has been used for the electronic potential energies and their gradients and the DZP basis set for the second derivatives of the electronic potential surfaces 'A' or 'C', respectively. For the surfaces 'B' only the TZ2P basis set and for 'D' only the DZP basis were employed, respectively.

3.3 The Functionals

In order to determine which of the various functionals commonly used in DFT calculations might be the most appropriate for trichlorofluoromethane the geometries and the harmonic frequencies were determined for 9 functionals with the TZ2P basis set. LDA [41], BLYP [27], B3LYP [42], B97-1 [43], BP86 [26], PBE [44], PBE0 [31], HCTH/93 [45] and the HCTH/407 functional [46] yielded all satisfying results. The corresponding values are given in Tables 3.1 and 3.2. The experimental geometries are taken from ref. [47]. Tables 3.1 and 3.2 also give harmonic wavenumbers and geometries for the B3LYP functional with the 6-311+G* basis [4, 48] and the B97-1 functional with the DZP basis. Experimental values of the fundamentals are taken from [4] and [49].

Geometries

The determined geometries indicate in a manner the suitability of a given functional/basis set for the considered molecular system. The geometry is so important since in general for the calculation of the potential energy hyper surface the BORN-OPPENHEIMER approximation is used. In order to calculate precise transition frequencies, accurate geometries must be predicted. For all the functionals listed in table 3.1 the predicted values for the C-F bond length were about 10 pm too short and C-Cl bond lengths were a little bit too long. It is not surprising that the angular predictions are within 1 degree of the T_d angle 109.47° which is enforced by the CADPAC input.

Table 3.1: Comparison of experimental values for the geometries with results of DFT calculations with eleven different functionals using all the TZ2P basis unless otherwise indicated

functional	r(C-F) [Å]	r(C-Cl) [Å]	\angle Cl-C-Cl [°]	\angle Cl-C-F [°]
LDA	1.332	1.762	110.35	108.65
BLYP	1.358	1.807	110.45	108.47
B3LYP	1.341	1.784	110.44	108.49
B97-1	1.339	1.786	110.43	108.49
BP86	1.351	1.790	110.35	108.58
PBE	1.351	1.786	110.35	108.58
PBE0	1.335	1.766	110.33	108.60
HCTH/93	1.342	1.781	110.35	108.57
HCTH/407	1.342	1.773	110.43	108.50
B3LYP(6-311+G*) [48]	1.351	1.785	110.91	107.99
B97-1(DZP)	1.339	1.786	110.43	108.49
experimental [47]	1.44 ± 0.04	1.76 ± 0.02	113 ± 3	100 ± 0.1

Table 3.2: Experimental fundamentals and calculated harmonic transition wavenumbers in cm^{-1} for eleven DFT functionals with the TZ2P basis unless otherwise indicated. First non degenerate values, then degenerate values are given in decreasing energy.

functional	ω_1	ω_4	ω_7	ω_2	ω_3	ω_5	ω_6	ω_8	ω_9
LDA	1079.104	532.238	342.936	799.543	799.536	390.905	390.903	236.808	236.806
BLYP	991.649	488.422	324.881	729.023	728.960	367.265	367.249	228.213	228.213
B3LYP	1068.297	519.184	342.203	794.709	794.662	389.750	389.732	240.038	240.028
B97-1	1090.990	526.884	342.479	812.016	811.983	393.561	393.560	239.244	239.240
BP86	1022.428	505.818	332.495	759.345	759.321	376.780	376.771	231.623	231.618
PBE	1026.048	511.125	334.711	767.595	767.567	379.314	379.312	232.817	232.812
PBE0	1113.300	542.977	351.969	839.384	839.338	402.169	402.150	245.325	245.323
HCTH/93	1045.126	513.362	339.722	771.397	771.374	384.824	384.815	238.161	238.160
HCTH/407	1044.213	519.674	344.387	780.772	780.677	388.470	388.444	241.589	241.550
B3LYP(6-311+G*) [4]	1061.91	522.17	347.94	805.82		394.12		245.53	
B97-1(DZP)	1121.831	537.384	351.435	843.240	843.239	400.621	400.621	245.168	245.167
fundamental	ν_1	ν_4	ν_7	ν_2	ν_3	ν_5	ν_6	ν_8	ν_9
experimental [4, 49]	1081.27982	538.16	351.41	849.52857		399.2		244.1	

Harmonic wavenumbers

Nearly all the calculated harmonic frequencies ω_i of all the functionals are lower than the observed fundamentals ν_i with the exception of PBE0 and B97-1, underlining the already mentioned bond length inadequacy. If we compare for illustration three harmonic frequencies calculated with the well known functional BLYP with the corresponding experimentally determined fundamentals:

- $\omega_1 - \nu_1 = -90 \text{ cm}^{-1}$,
- $\omega_4 - \nu_4 = -50 \text{ cm}^{-1}$
- $\omega_2 - \nu_2 = -120 \text{ cm}^{-1}$.

In comparison to that the PBE0 functional gives a great improvement with much smaller absolute values of the corresponding differences:

- $\omega_1 - \nu_1 = 32 \text{ cm}^{-1}$,
- $\omega_4 - \nu_4 = 5 \text{ cm}^{-1}$
- $\omega_2 - \nu_2 = -10 \text{ cm}^{-1}$.

Even though it is clear that the experimental fundamentals are not expected to be equal to the harmonic wavenumber because they do not yet take into account the anharmonic contributions. However, the difference is far too large and often even of the wrong sign. Meaning that it is easier to decrease the result for the harmonic frequency by introducing anharmonicity than to increase it. Table 3.2 gives the harmonic frequencies for $\text{C}^{35}\text{Cl}_3\text{F}$ using in the CADPAC calculations a C_s symmetry whereas the true symmetry is C_{3v} . C_s symmetry is used in order to obtain as an output which is appropriate as an input for MULTIMODE. It is very encouraging that for PBE0 the results of the three pairs of degenerate modes are degenerate to within 0.05 cm^{-1} .

Used functionals for the surface calculations

PBE0 was chosen to be used for all crucial calculations of surface 'A' (i.e. potential energies and their gradients) and for all calculations of surface 'B'. It gives the shortest C-Cl bondlengths and differs the least in its harmonic wavenumbers from experimental fundamental frequencies. LDA also yielded very short C-Cl bondlengths. But as already discussed in chapter 2.1.2. 'Functionals in DFT' the Local Density Approximation functional describes only poorly molecular properties because it considers the electronic density to be homogeneous throughout the whole molecule. This shows to be true if one inspects the harmonic wavenumbers calculated by LDA:

they are much smaller than the experimental fundamentals and deviate significantly from the values obtained by hybrid functionals. Interestingly the famous BLYP functional yields harmonic wavenumbers which are even worse than for LDA. In order to measure the effects of using a different kind of functional also the hybrid B97-1 functional is investigated in this work.

However, the fact that even for PBE0 the C-Cl bond length is not smaller than the experimental value and that the harmonic wavenumber ω_4 is smaller than the experimental ν_4 indicates already at this point that the results of the calculations with normal modes which involve vibrations with C-Cl motion might become problematic. An introduction how to recognize which normal modes involve which intra molecular motion within cartesian coordinates is given in the next section.

3.4 The l-matrix

The l-matrix was already mentioned in chapter 2.3.1. and introduced in 2.3.2. Its basic idea is to "focus" the simultaneous changing of all the nuclei in a given molecular system within a given vibration on one coordinate: the normal mode Q . If the potential energy surface were perfectly harmonic each displacement in a given normal coordinate would correspond to a motion of the nuclei in a local potential energy minimum with respect to the other normal modes as long as all other normal modes are kept zero. So, the l-matrix is the essential link between the molecular structure in cartesian coordinates and the normal coordinate Q . The l-matrix describes the relative amplitude of displacement from equilibrium geometry (compare to table (3.1)) for each nucleus for each normal mode being normalized to 1. Therefore the elements of the l-matrix have to fulfill for each vibrational degree of freedom the normalization condition that $\sum_{xyz,\alpha} l_{xyz,\alpha,i}^2 = 1$ where i is a given vibrational degree of freedom, α runs over the nuclei in the molecule and xyz over all the three cartesian coordinates: $l_{xyz} = l_x + l_y + l_z$.

CADPAC generates the l-matrix for each harmonic frequency. However, in order to have the necessary formal C_s input for MULTIMODE also the frequencies had to be calculated within C_s -symmetry. Numerical inaccuracies were thus introduced into the l-matrix which were of the order of less than a percent. The l-matrix was then changed manually to C_{3v} by setting values of symmetric motions equal. Thus symmetrical accuracy was obtained again while orthogonality was lost. However, since the inaccuracies are neglectible small the l-matrix was not orthogonalized again. One obtains for ω_6 for example: $\sum_{xyz,\alpha} l_{xyz,\alpha,6}^2 = 1.000028$ instead of 1. The symmetry of a given mode becomes evident by inspection of the elements in the l-matrix of the corresponding mode. The reference system of the molecule in cartesian coordinates is shown in figure 3.1. The equilibrium geometry is given in table 3.3. One can thus identify the corresponding vibrational normal modes of CCl_3F .

Table 3.3: Equilibrium geometry in atomic units for $\text{C}^{35}\text{Cl}_3\text{F}$ calculated by PBE0 and TZ2P basis.

Atom	x	y	z
C1	0.0000000000	0.0000000000	0.0314423666
F1	0.0000000000	0.0000000000	2.5494624038
Cl1	-1.5811556929	2.7386419948	-1.0326586121
Cl2	-1.5811556929	-2.7386419948	-1.0326586121
Cl3	3.1623113858	0.0000000000	-1.0326586121

Figure 3.1: CCl_3F in a right handed cartesian coordinate reference system: the z-axis points up while we look down from F towards C. The positions of the atoms correspond to table 3.3

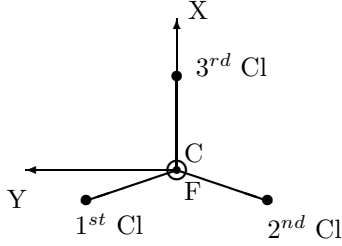


Table 3.4: The l-matrix. All fundamental frequencies ω_i of a given normal mode i are in cm^{-1} . The coordinate system corresponds to figure 3.1. For each normal mode the deduced irreducible representation is indicated.

$\Gamma_{C_s}^{rrr}$	i	ω_i	atom	x	y	z
A'	1	1091.04	C	0.00000	0.00000	0.81216
			F	0.00000	0.00000	-0.58285
			Cl	-0.00083	0.00148	-0.01537
			Cl	-0.00083	-0.00148	-0.01537
			Cl	0.00166	0.00000	-0.01537
A''	2	812.11	C	0.00000	0.94276	0.00000
			F	0.00000	-0.16419	0.00000
			Cl	0.07185	-0.18518	0.02880
			Cl	-0.07185	-0.18518	-0.02880
			Cl	0.00000	-0.06085	0.00000
A'	3	812.05	C	0.94276	0.00000	0.00000
			F	-0.16419	0.00000	0.00000
			Cl	-0.10242	0.07185	-0.01665
			Cl	-0.10242	-0.07185	-0.01665
			Cl	-0.22649	0.00000	0.03323
A'	4	526.91	C	0.00000	0.00000	0.39234
			F	0.00000	0.00000	0.56685
			Cl	-0.17906	0.31022	-0.21590
			Cl	-0.17906	-0.31022	-0.21590
			Cl	0.35824	0.00000	-0.21590
A''	5	393.54	C	0.00000	-0.05421	0.00000
			F	0.00000	0.66736	0.00000
			Cl	0.26646	-0.30720	0.31400
			Cl	-0.26646	-0.30720	-0.31400
			Cl	0.00000	0.15428	0.00000
A'	6	393.53	C	-0.05421	0.00000	0.00000
			F	0.66736	0.00000	0.00000
			Cl	0.00000	0.26664	-0.18119
			Cl	0.00000	-0.26664	-0.18119
			Cl	-0.46078	0.00000	0.36267
A'	7	342.54	C	0.00000	0.00000	-0.31336
			F	0.00000	0.00000	-0.44629
			Cl	-0.22643	0.39200	0.17096
			Cl	-0.22643	-0.39200	0.17096
			Cl	0.45309	0.00000	0.17066
A'	8	239.29	C	0.12762	0.00000	0.00000
			F	0.39817	0.00000	0.00000
			Cl	-0.36350	-0.41702	-0.11868
			Cl	-0.36350	0.41702	-0.11868
			Cl	0.35877	0.00000	0.23737
A''	9	239.26	C	0.00000	-0.12762	0.00000
			F	0.00000	-0.39817	0.00000
			Cl	0.41696	-0.11797	-0.20561
			Cl	-0.41696	-0.11797	0.20561
			Cl	0.00000	0.60424	0.00000

3.5 Asymmetric Top versus Symmetric Top

As already introduced in chapter 2.2.2 one has to transform the anharmonic constants obtained by SPECTRO within the asymmetric top description in the case of the C_{3v} isotopomers. One can show that $x_{ss'}^{sym} = x_{ss'}^{asym}$ and that $x_{sta}^{asym} \cong x_{stb}^{asym}$ which leads to the conclusion that $x_{st}^{sym} = 1/2(x_{sta}^{asym} + x_{stb}^{asym})$ ([50]). This can easily be checked by inspection of the SPECTRO output (see Appendix A). In order to express $x_{tt'}^{sym}$ and $g_{tt'}^{sym}$ and their corresponding g constants in terms of the anharmonic constants of the asymmetric top description the in chapter 2.2.2 introduced method of simply subtracting the HAMILTONIANS has been used. In the following this approach will be called 'HAMDIF'. A derivation had been done in ref. ([50]) for benzene. In Appendix A the equations are checked with the help of MATHEMATICA for any C_{3v} symmetric molecule. It is found that:

$$\begin{aligned}
 x_{tt}^{sym} &= x_{tata}^{asym} \\
 g_{tt} &= \frac{1}{2}x_{tatb}^{asym} - x_{tata}^{asym} \\
 x_{tt'}^{sym} &= \frac{1}{2}(x_{tata'}^{asym} + x_{tatb'}^{asym}) \\
 g_{tt'} &= \frac{1}{2}(x_{tata'}^{asym} - x_{tatb'}^{asym})
 \end{aligned} \tag{3.1}$$

Except for $g_{tt'}$ these expressions have been identified likewise in ([50]) for the D_{6h} symmetric molecule benzene. $g_{tt'}$ has not yet been explicitly given in those simple terms of x^{asym} . These expressions to transform anharmonic constants obtained by an asymmetric top HAMILTONIAN into anharmonic constants corresponding to a symmetric top HAMILTONIAN have been implemented in a small FORTRAN program which uses the SPECTRO output as input. It is given in Appendix A.

However, the result is somewhat surprising. One would expect intuitively that x_{tt}^{sym} should contain some x_{tatb}^{asym} . Furthermore, it is found by MATHEMATICA that these identifications are true if and only if x_{tata}^{asym} is equal to x_{tatb}^{asym} . That this is not the case can be found by inspection of the results of SPECTRO for the x_{tata}^{asym} of the symmetric top isotopomers and also by recognizing that in this case all $g_{tt'}$ would have to be equal zero.

Alternatively, for the two symmetric top isotopomers all anharmonic constants between degenerate modes can be recalculated with the help of the eigenvalue spectrum which is given in the SPECTRO output. In the following this approach will

be called 'SPEC'. The following expressions are used:

$$x_{tt} = \frac{(n_t \nu_t)^{(A_1)} - n_t \nu_t}{n_t} = \frac{(2\nu_t)^{(A_1)} - 2\nu_t}{2} \quad (3.2)$$

$$g_{tt} = \frac{(n_t \nu_t)^{(E)} - (n_t \nu_t)^{(A_1)}}{l_t^2} = \frac{(2\nu_t)^{(E)} - (2\nu_t)^{(A_1)}}{4} \quad (3.3)$$

$$x_{tt'} = \frac{(n_t \nu_t + n_{t'} \nu_{t'})^{(A_1)} - n_t \nu_t - n_{t'} \nu_{t'}}{n_t + n_{t'}} = \frac{(1\nu_t + 1\nu_{t'})^{(A_1)} - 1\nu_t - 1\nu_{t'}}{2} \quad (3.4)$$

$$\begin{aligned} g_{tt'} &= \frac{(n_t \nu_t + n_{t'} \nu_{t'})^{(E)} - (n_t \nu_t + n_{t'} \nu_{t'})^{(A_1)}}{l_t \cdot l_{t'}} \\ &= \frac{(1\nu_t + 1\nu_{t'})^{(E)} - (1\nu_t + 1\nu_{t'})^{(A_1)}}{1} \end{aligned} \quad (3.5)$$

Here n_t and l_t are the corresponding quantum numbers. Having one quanta in each mode there are four combinations:

l_t	$l_{t'}$	$\Gamma_{C_{3v}}^{irr}$
+1	-1	A_1/A_2
-1	+1	A_1/A_2
+1	+1	E
-1	-1	E

Since for E the quantum numbers l_t and $l_{t'}$ have the same sign the denominator in eq. (3.5) will always be positive. Unfortunately, it is not always evident how to determine the x^{sym} from an eigenvalue spectrum which has been predicted by an asymmetric top HAMILTONIAN. For example x_{22} , g_{22} , x_{58} and g_{58} of $C^{35}Cl_3F$ are calculated as follows:

$$\begin{aligned} (2\nu_2)^{(A_1)} &= 1647.1662 \text{ cm}^{-1} \\ 2(\nu_2) &= 2 \cdot \frac{827.0915 + 827.4308}{2} = 1654.5223 \text{ cm}^{-1} \\ x_{22} &= \frac{1647.1662 - 1654.5223}{2} = -3.68 \text{ cm}^{-1} \end{aligned}$$

where 827.0915 and 827.4308 cm^{-1} are the two degenerate components ν_2 and ν_3 . There is thus an estimated error of $\Delta_{x_{22}} \approx \pm 0.15 \text{ cm}^{-1}$. Concerning g_{22} :

$$\begin{aligned} (2\nu_2)^{(E)} &= \frac{1653.1534 + 1647.9301}{2} = 1650.5 \text{ cm}^{-1} \\ g_{22} &= \frac{1650.54175 - 1647.54815}{4} = 0.74840 \text{ cm}^{-1} \end{aligned}$$

Having a considerable error of $\Delta_{g22} \approx \pm 0.7 \text{ cm}^{-1}$! The averaged values indicate thus in a way the error for the numerical inaccuracies which are introduced by ignoring symmetry when deducing the effective HAMILTONIAN. Wishing to determine the overtones ($2\nu_2$) one encounters the following SPECTRO output:

```
4126.7247 1647.1662 NON-DEG (Vs) : 0 0 2 0 0 0 0 0 0
4127.4885 1647.9301 NON-DEG (Vs) : 0 2 0 0 0 0 0 0 0
4132.7119 1653.1534 NON-DEG (Vs) : 0 1 1 0 0 0 0 0 0
```

The first column indicates the energy in cm^{-1} , the second the energy above zero point, the third the degeneracy of the state (in the asymmetric top expression there is no degeneracy for CCl_3F) and the final nine numbers represent the vibrational quanta in the following (energetical) order which corresponds to the order shown in table 3.4: n_1^{asym} , $n_{2_{deg}}^{asym}$, $n_{3_{deg}}^{asym}$, n_4^{asym} , $n_{5_{deg}}^{asym}$, $n_{6_{deg}}^{asym}$, n_7^{asym} , $n_{8_{deg}}^{asym}$, $n_{9_{deg}}^{asym}$. In table 3.4 is also indicated the symmetry of the corresponding normal mode from which the symmetry of vibrational state given within SPECTRO can be deduced. For example the state

normal mode	1	2	3	4	5	6	7	8	9
$\Gamma_{C_s}^{irr}$	A'	A''	A'	A'	A''	A'	A'	A'	A''
vibrational state	0	1	1	0	0	0	0	0	0

would correspond to a vibrational state having the irreducible representation $\Gamma^{irr} = A''$ (within the C_s symmetry group).

Thus, we find for the output above:

$$\begin{array}{cccccccccc|l} 1647.1662 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & A' \\ 1647.9301 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & A' \\ 1653.1534 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & A'' \end{array}$$

and state that the degenerate E state must be formed by the A'' plus that A' which is the closest to the A'' which is in this case the $1647.9301 \text{ cm}^{-1}$ band. The remaining A' state is defined to be A_1 . Of course, this means that also here there enters the approximation which has been affirmed by using the asymmetric top HAMILTONIAN since the A'' and A' states which are supposed to form the degenerate E state are not at all strictly degenerate. Imposing symmetry for the PES would have had the strict degeneracy of the A'' and one A' as a consequence.

In the case of the off diagonal anharmonic constants $_{58}$ the SPECTRO output is

```
3121.1127 641.5542 NON-DEG (Vs) : 0 0 0 0 1 0 0 1 0
3121.1851 641.6267 NON-DEG (Vs) : 0 0 0 0 0 1 0 0 1
3121.4750 641.9166 NON-DEG (Vs) : 0 0 0 0 1 0 0 0 1
3121.4995 641.9411 NON-DEG (Vs) : 0 0 0 0 0 1 0 1 0
```

which corresponds to

$$\begin{array}{cccccccccc|l} 641.5542 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & A'' \\ 641.6267 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 & A'' \\ 641.9166 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & A' \\ 641.9411 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & A' \end{array}$$

It is difficult to judge which of the four possible combinations of $A''+A'$ states will form the E state. If the numerical inaccuracy of the anharmonic constants determining the eigenvalue spectrum is taken into account it might facilitate a choice: $x_{55}^{asym} = -0.435$, $x_{66}^{asym} = -0.401$. As deviations to it we find ± 0.019 for 55/66 and ± 0.0035 for 88/99. By adding the corresponding corrections to the eigenvalues we find the following:

$$\begin{array}{cccccccccc|l} 641.5352 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & A'' \\ 641.6457 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 & A'' \\ 641.9131 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & A' \\ 641.9446 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & A' \end{array}$$

The values did not change considerably which as above indicates the missing symmetry in the PES. However, the two closest lying A'' and A' states should rather form the degenerate E state within the symmetric top representation than the alternative combination. A transition towards the remaining A'' state (becoming A_2 within a symmetric top) is symmetry forbidden when leaving from a symmetric groundstate. Since it is not intended to change the eigenvalue spectrum the uncorrected values are still used to determine the off diagonal anharmonic constants x_{58} and g_{58} :

$$\begin{aligned} (\nu_5 + \nu_8)^{(A_1)} &= 641.9411 \text{ cm}^{-1} \\ \nu_5 &= \frac{398.3835 + 398.3911}{2} = 398.3873 \text{ cm}^{-1} \\ \nu_8 &= \frac{243.5446 + 243.5575}{2} = 243.55105 \text{ cm}^{-1} \\ x_{58} &= \frac{641.9411 - 398.3873 - 243.55105}{2} \approx 0.0014 \text{ cm}^{-1} \\ \text{and} \\ (\nu_5 + \nu_8)^{(E)} &= \frac{641.6267 + 641.9166}{2} = 641.7718 \text{ cm}^{-1} \\ g_{58} &= \frac{641.7718 - 641.9411}{1} \approx -0.17 \text{ cm}^{-1} \end{aligned}$$

All other degenerate/degenerate anharmonic constants have been determined in the

same manner: Assuming that the mean value of the two closest lying levels of different symmetry corresponds to the E state. The deviation of the original values from the mean value is considered to correspond to an estimated error.

3.6 The Coupling Approach

3.6.1 Potential Energy within the Coupling Approach

Having defined the polynomial series expansions f_i , f_{ij} and f_{ijk} as in eq. (2.99-2.101) a potential energy dependent only on three normal modes would be expressed as in the following:

$$\begin{aligned}
 V(Q_1, Q_2, Q_3) = & \sum_{i=1}^3 f_i(Q_i) + \sum_{i=1}^3 Q_i \sum_{j=1}^3 f_{ij}(Q_j)(1 - \delta_{ij}) \\
 & + \sum_{i=1}^3 Q_i \sum_{j=1}^3 Q_j (1 - \delta_{ij}) \sum_{k=1}^3 f_{ijk}(Q_k)(1 - \delta_{jk})
 \end{aligned} \tag{3.6}$$

The potential energy which has been finally used corresponds to the above expression but the sums go from $i = 1$ to 9 since there are nine normal modes in CCl_3F .

3.6.2 Inspection of the fit

For some of the expressions which are deduced within the Coupling Approach predictions are possible for reasons of symmetry. They are derived in this section.

For a C_s -symmetry there are modes with: A' and A'' symmetry. The former represents symmetric behaviour with respect to the reflection plane, the latter represents asymmetric behaviour.

It is recalled that the following equations are valid (being already used in chapter 2.2.2 and 3.5):

$$\begin{aligned}
 A'' \times A'' &= A' \\
 A' \times A' &= A' \\
 A'' \times A' = A' \times A'' &= A''
 \end{aligned}$$

In the C_{3v} symmetric isotopomers of CCl_3F there are three degenerate modes of which each one has one component with A'' -symmetry.

By expressing the potential energy as it is done within the Coupling Approach it is necessary that all terms are of A' symmetry. Therefore predictions to the kind of exponents of the series expansions (f_{ij}) approaching the derivatives in eq. (2.99) etc. can be done. Their multiplication with other modes must obey the symmetry rules stated above. There are four possible combinations for the coupling of two normal modes: Coupling of two asymmetric, coupling of two symmetric, coupling of an asymmetric with the derivative of a symmetric and coupling of a symmetric

with the derivative of an asymmetric normal mode. Defining the derivative with respect to Q as $\partial_Q = \frac{\partial}{\partial Q}$ and denoting the A'' modes u and all A' normal modes g one obtains thus for f_{gu}, f_{ug}, f_{uu} and f_{gg} (note that $f_{gu} \neq f_{ug}$):

1. $Q_g \partial_{Q_g} V(Q_u)$ has to be of A' symmetry. Since by definition Q_g is of A' symmetry it follows

$$\text{that } \partial_{Q_g} V(Q_u) = A'$$

So, the series expansion f_{gu} to describe $\partial_{Q_g} V(Q_u)$ is expected to have even exponents.

2. Also $Q_u \partial_{Q_u} V(Q_g)$ must be A' .

$$\text{Therefore } \partial_{Q_u} V(Q_g) = A''$$

This expression is contradictive. This is so because $\partial_{Q_u} V(Q_g)$ is a function of Q_g which is A' and not A'' . Therefore f_{ug} has to be equal to zero.

3. The combination $Q_u \partial_{Q_u} V(Q_u) = A'$ is the case in which $\partial_{Q_u} V(Q_u)$ has to be expanded within an uneven polynom f_{uu} of A'' symmetry.
4. The combination $Q_u \partial_{Q_u} V(Q_u)$ tells then that $\partial_{Q_u} V(Q_u)$ can be represented by uneven as well as by even series expansion f_{gg} .

Chapter 4

Results

All obtained PES and how they are constituted are presented in this part of the study.

4.1 An overview

In table 4.1 are indicated the various PES used in this work, the isotopomers, the spectroscopic programs, DFT functionals, basis sets, approximations and tables where the corresponding results are presented are indicated.

Table 4.1: The PES of this work

PES	Isotopomer	Program	Functional/Basis set	Coupling Approach	table
'A'	C ³⁵ Cl ₃ F	MM	PBE0/TZ2P—B97-1/DZP	yes	5.1, 5.3
'D'	C ³⁵ Cl ₃ F	MM	B97-1/DZP	no	5.3
'B'	C ³⁵ Cl ₃ F	SP	PBE0/TZ2P	no	5.3
'B'	C ³⁷ Cl ³⁵ Cl ₂ F	SP	PBE0/TZ2P	no	5.3
'B'	all	SP	PBE0/TZ2P	no	5.8,5.5
'C'	C ³⁵ Cl ₃ F	SP	PBE0/TZ2P—B97-1/DZP	yes	5.3, 5.4 - 5.5

In the following sections the results for each PES are explained in more detail.

4.2 MULTIMODE

4.2.1 Surface 'A'

The electronic potential energy, its first and second derivatives were evaluated for 16 displacements along each normal mode and such for a total of 144 geometries

(taking already into account energetically symmetrical normal modes). The electronic potential energy and the gradients were obtained with the TZ2P basis set, and the B97-1 or the PBE0 functional, respectively. The second derivatives with the DZP basis are only calculated for B97-1. Thus, following the outline in chapter 2.3. 'the Coupling Approach' the electronic potential energies account for eq. (2.102) representing thus $V^{(1)}$. The gradients define eq. (2.103) and thus a part of $V^{(2)}$ and the second derivatives were fitted by eq. (2.104) corresponding to $V^{(3)}$ and the remaining part of $V^{(2)}$. The used expression of the potential energy is:

$$V(\mathbf{Q}) = V_{PBE0,TZ2P}^{(1)energies} + V_{PBE0,TZ2P}^{(2)gradients} + V_{B97-1,DZP}^{(2)2ndDerivatives} + V_{B97-1,DZP}^{(3)2ndDerivatives}$$

The variational calculations of MULTIMODE followed the procedure described in [13, 51]. For the VSCF calculations, 8 basis functions are used per normal mode starting from 14 primitives harmonic oscillator functions and the 16 Gauss quadrature points per normal mode are contracted to 10 points. The contraction technique is described in detail in ref. [13, (a)]. In the VCI calculations, convergency is reached with the following CI basis: The excitations from the vibrational VSCF ground state involve up to a maximum of 4 normal modes simultaneously. For the one-, two-, three- and four- mode excitations, the maximum of quanta per mode is 6, 5, 4 and 3, respectively, and the maximum sum of quanta per vibrational level is 6. The same number of primitive functions and integration points as in the VSCF step are used, and 7 contracted basis functions being necessary. Predictions for fundamentals, combination bands and overtones of $C^{35}Cl_3F$ from MULTIMODE VSCF and VCI calculations using surface 'A' are presented in Table 5.3.

The calculation time for the electronic potential energy and its first derivative was about 20 min on the machines in Zürich, the time for the second derivatives was the double: 40 min even though a smaller basis had been chosen (DZP). Thus for generating the total PES 'A' consisting of 144 points approximately only 6 d of calculations were necessary.

4.2.2 Surface 'D'

To investigate the validity of PES 'A' a higher dimensional PES ('D') was generated for $C^{35}Cl_3F$. This PES consists of a grid of all possible combinations of single point calculations for two normal modes. The total number of points for the nine modes is thus: $n^D * \sum_{i=2}^N$ where n is the number of single point calculations per normal mode, D is the dimensionality of the PES and N is the number of vibrational degrees of freedom. Thus for $n = 10$, $N = 9$ and a 2D PES there are $100 * (9 + 8 + 7 + 6 + 5 + 4 + 3 + 2) = 3400$ points to be calculated.

For all combinations, however, in which a degeneracy is involved the $V(Q_{degenerate})$ has to be symmetric for the A'' -mode (mode 9, 5 and 1 - compare to the section 'Inspection of the fit'). Therefore only half of the given 2D surface needed to be evaluated and then reflected to give the complete two normal mode dependent surface. Such the total number of points not lying on a single normal mode was only 2550 points. Using the information of those points which led already to PES 'A' resulted in a total number of 2694 geometries for which energies and gradients are determined. All the 2550 points were calculated with the B97-1 functional and the DZP basis set. The energies and gradients were used in a two-dimensional Hermite interpolation to obtain the PES 'D' (see reference [18]). The results for the fundamentals are shown in table 5.3.

Because one point on this PES and its gradient takes about 280 seconds the total PES 'D' with 2550 needed nearly 8 d of calculation time on the machines in Zürich.

4.3 SPECTRO

The second derivatives which are the elements of the HESSIAN matrix and figure in eq. (Vspectro), (phiiijk) and (phiiiijj) are approached in this present study by two alternative ways:

1. They can be determined with the help of a force field which is directly calculated by a combined SPECTRO / CADPAC code using the energies of 19 points. This is done for all isotopomers. The PES using these expressions is called 'B'. It is generated for all isotopomers.
2. They are derived from equations (2.102), (2.103) and (2.104) (see section 2.3) defining surface 'A' (compare to the chapter 'The Coupling Approach'). The surface using these definitions of the quartic and cubic terms is called 'C'. As 'A' it is only derived for the isotopomer C³⁵Cl₃F.

4.3.1 Surface 'B'

Surface 'B' was determined by a SPECTRO / CADPAC calculation [14] using the functional PBE0 and the TZ2P basis set. To generate a 'B' PES for one isotopomer circa 2,5 d calculation time on the machines in Zürich was needed. For the isotopomers C³⁵Cl₃F, C³⁷Cl₃F, C³⁵Cl₂³⁷ClF and C³⁵Cl³⁷Cl₂F vibrational eigenvalues, harmonic frequencies, anharmonic constants, absorption intensities and rotational constants are shown in tables 5.3 and 5.8, 5.5. According to eq. (2.87) the absorption intensities were corrected by weighting with their BOLTZMANN factors for $T = 298 \text{ K}$ [7]:

$$1 - g_i \exp\left[-\frac{h c \nu_i}{k T}\right] = 1 - g_i \exp\left[-0.004828 \nu_i / \text{cm}^{-1}\right] =$$

- 0.9946 for $\nu_1 = 1080.7 \text{ cm}^{-1}$, $g_i = 1$
- 0.9247 for $\nu_2 = 535.6 \text{ cm}^{-1}$, $g_i = 1$
- 0.8147 for $\nu_3 = 349.2 \text{ cm}^{-1}$, $g_i = 1$
- 0.9668 for $\nu_4 = 848.9 \text{ cm}^{-1}$, $g_i = 2$
- 0.7037 for $\nu_5 = 395.9 \text{ cm}^{-1}$, $g_i = 2$
- 0.6211 for $\nu_6 = 242.2 \text{ cm}^{-1}$, $g_i = 2$

As already mentioned in chapter 2.2.2 and 3.5 there are approximations for the C_{3v} symmetric isotopomers. Their anharmonic constants x_{st}^{sym} , x_{tt}^{sym} , g_{tt}^{sym} , $x_{tt'}^{sym}$, or

$g_{tt'}^{sym}$, respectively, have to be deduced from the asymmetric top expression $x_{st_a}^{asym}$, $x_{st_b}^{asym}$, $x_{t_a t_a}^{asym}$, $x_{t_b t_b}^{asym}$ and $x_{t_a t_b}^{asym}$. Within the 'HAMDIF' method this is done in detail in Appendix A with the help of the formulas (3.1) introduced in chapter 3.5. Furthermore, following the 'SPEC' method the anharmonic constants for the symmetric top isotopomers are also obtained by calculating them with the help of the eigenvalue spectrum generated by the anharmonic constants of the asymmetric top representation (see chapter 3.5, expressions 3.2 -3.5). The spectrum is likewise already given in the SPECTRO output. The latter approach to determine the anharmonic constants is not as elegant as expressing directly $x^{sym}=f(x^{asym})$ but it avoids the problem of correlating quantum numbers of different symmetrical representations. Both ways of determining the symmetric top anharmonic constants are carried out in order to see if the idea of expressing directly $x^{sym} = f(x^{asym})$ introduces any non negligible errors.

4.3.2 Surface 'C'

For $C^{35}Cl_3F$ the harmonic force constants were identified not within the SPECTRO / CADPAC-calculation but also with the potential of the Coupling Approach (see above). The cubic and quartic force constants were derived by finite displacement using the normal SPECTRO calculation. Thus all the spectroscopic constants became accessible via the Coupling Approach. No further calculation time was needed for these results.

Chapter 5

Discussion, Conclusions and Outlook

In this chapter the actual results are presented and discussed. Finally, conclusions are drawn and potential improvements are proposed.

5.1 Discussion

Discussing the Coupling Approach: Table 5.1

Table 5.1 represents the dependency of the fundamental wavenumbers on the increasing order of coupling in the expression for the potential energy (see eq. (2.54) and (2.99) and the following). Thus in table 5.1 $V^{(1)}$ means that the potential energy surface is approximated as $V(\mathbf{Q}) = \sum_{i=1}^9 V^{(1)}(Q_i)$ while $V^{(1)} + V^{(2)}$ means that $V(\mathbf{Q}) = \sum_{i=1}^9 V^{(1)}(Q_i) + \sum_{i=1, i \neq j}^9 V^{(2)}(Q_i, Q_j)$ etc.. Going from first to third order one observes generally an improvement of several cm^{-1} in comparison to experiment. Furthermore, also the degeneracy improves. The largest improvement takes place if the coupling between all the combinations of two normal modes is included. However, the improvement due to the including of simultaneous coupling between three modes is neglectible. So, this means that for CCl_3F the quality of the basis set and the functional which introduce f_{ijk} (eq. 2.101) within the Coupling Approach is not crucial and that only the gradient and the energies are essential within the Coupling Approach. Thus the calculation time could become one third of what it takes originally. By achieving this state of computational cost (~ 2 d) the Coupling Approach becomes even cheaper than the standard procedure to generate PES 'B' ($\sim 2,5$ d).

Table 5.1: Comparison of the convergence by varying the degree of coupling in the potential energy expansion in the frame of the Coupling Approach: Variation of the MM-VSCF fundamentals [cm^{-1}] of $\text{C}^{35}\text{Cl}_3\text{F}$

ν_i	$V^{(1)}$	$V^{(1)} + V^{(2)}$	$V^{(1)} + V^{(2)} + V^{(3)}$	exp. ([49])
ν_1	1095.38	1091.83	1091.69	1081.27982
ν_4	542.06	539.91	539.92	538.16
ν_7	351.87	350.30	350.36	351.41
ν_2	838.34	830.13	830.53	849.53
ν_3	842.74	831.10	831.13	"
ν_5	402.34	399.46	399.49	399.2
ν_6	402.60	399.49	399.49	"
ν_8	245.54	244.08	244.09	244.1
ν_9	245.28	243.97	244.00	"

Discussion of the eigenvalues in Table 5.2 and 5.3

All results in table 5.3 compare very well to experimental values. The agreement with experiment is excellent for nearly all fundamentals and low lying combination bands: often even less than 1 cm^{-1} . The degenerate CCl_3 stretching normal mode ν_4 and the ν_1 C-F stretching normal mode could be satisfyingly calculated disagreeing with respect to experiment by $\approx 22 \text{ cm}^{-1}$ and $\approx 11 \text{ cm}^{-1}$, respectively. These are the two highest lying fundamentals. It is therefore consistent that the agreement achieved for the corresponding overtones as for example the $2\nu_1$ band is not any better.

As already mentioned in Chapter 3.3 'The Functionals' the used functionals might not be the most appropriate in order to calculate the ν_4 CCl vibration because the calculated harmonic wavenumber is too low and the CCl bondlength is too long. So, one would not expect an agreement with experiment as good as for the other fundamentals. However, considering this band and the ν_1 it becomes clear that it is reproduced the best by the 'C'-surface which represents the Coupling Approach combined with SPECTRO.

Thus we can conclude that the reason for the comparatively less accurate prediction must be rather due to the potential energy calculations than due to the fitting procedures which generate the input for MULTIMODE or SPECTRO

One observes a good agreement between the three surfaces 'A', 'B' and 'C'. They differ generally only between 0.5 and 2 cm^{-1} . Being computationally less expensive (see previous section) the Coupling Approach ('C') is directly comparable to

Table 5.2: Fundamentals ν_i and experimental values [49] (in cm^{-1}) determined for all isotopomers by PES 'B', for $\text{C}^{35}\text{Cl}_3\text{F}$ also by 'C'

i	'C': $\text{C}^{35}\text{Cl}_3\text{F}$	'B': $\text{C}^{35}\text{Cl}_3\text{F}$	exp.	$\text{C}^{35}\text{Cl}_2^{37}\text{ClF}$	exp	$\text{C}^{35}\text{Cl}^{37}\text{Cl}_2\text{F}$	exp.	$\text{C}^{37}\text{Cl}_3\text{F}$	exp.
1	1093.3	1093.4	1081.9	1093.0	1080.7	1093.1	1079.9	1093.0	-
4	537.7	537.7	538.2	535.2	535.6	535.3	533.0	535.4	530.4
7	349.8	349.7	351.4	347.5	349.2	347.5	347.0	347.6	-
2	827.9	827.3	849.5	826.3	848.9	826.3	-	826.9	847.1
3	"	"	-	826.9	-	827.2	-	"	-
5	398.5	398.4	399.2	394.6	395.9	394.7	-	396.4	-
6	"	"	-	398.1	-	398.7	-	"	-
8	243.8	243.5	244.1	241.2	242.2	241.3	240.3	241.8	-
9	"	"	-	242.3	-	242.4	-	"	-

the conventionally obtained results of SPECTRO ('B'). Furthermore the influence of the use of MM instead of SPECTRO can be seen by comparison of the results for 'B' with the results for 'A'. Likewise they agree one with each other very well. Nevertheless, this good agreement is not the case for some overtones and combination bands like for example the A_1 absorption ($0001^11^10^0$): at $\approx 1225 \text{ cm}^{-1}$: $\nu(\text{PES 'A'}) - \nu(\text{PES 'B'}) = 3.6 \text{ cm}^{-1}$ or for the $2\nu_1$ ($2000^00^00^0$) band at 2145.2 cm^{-1} . Unfortunately, for the first and other diverging cases there is no experimental assignment in order to distinguish between these surfaces but the latter and the $\nu_1 + \nu_6$ absorption indicate for SPECTRO PES 'B' a slightly better agreement with experiment. The 'D'-surface behaves rather poor in comparison with the other surfaces. This means that the DZP-basis is insufficient and can even not be compensated by including 2D cuts into the PES (see also 4.3.2).

Nevertheless, this table demonstrates in general highly accurate predictions for relatively low calculation costs.

Also for $\text{C}^{35}\text{Cl}_2^{37}\text{ClF}$ the agreement between calculated vibrational frequencies and experimental data is splendid. Furthermore one can compare in table 5.3 the effect of the isotopic shift for experiment and the results for PES 'B'. The last column represents exactly the same approach towards the PES as the fifth. The only difference lies in symmetry. Thus the influence of change of symmetry from C_{3v} to C_s can be directly seen within the given approximations. The results show - in analogy to experiment - a shift of the eigenvalue spectrum towards lower vibrational frequencies. This is reasonable since the mass of one atom involved into the vibrational motion has been increased. Indeed a comparison of the predicted eigenvalues with the experimental ones allows to judge which of the two isotopomers is better described by the asymmetric top HAMILTONIAN. If the asymmetric HAMILTONIAN was inadequate for the symmetric isotopomer $\text{C}^{35}\text{Cl}_3\text{F}$ the differences of its eigenvalues

in comparison to experiment would be bigger than for the asymmetric isotopomer. The differences between these differences range in an order of less than 1 cm^{-1} meaning that they are small with respect to the systematical errors of the calculations. Thus, at least for the eigenvalue spectrum, the fact that the asymmetric top HAMILTONIAN has been used for a symmetric top molecule seems to be a "legitimate" approximation within the methods which were used in this work. The results for all isotopomers in table 5.2 demonstrate very good agreement of the predicted eigenvalues in comparison to experiment and correct tendencies for isotopic shifts from $\text{C}^{35}\text{Cl}_3\text{F}$ to $\text{C}^{37}\text{Cl}_3\text{F}$. The only exceptional result is the isotopic shift for $\text{C}^{37}\text{Cl}_3\text{F}$ for which the lowest eigenvalues are expected. However its ν_2 increases with respect to the lighter isotopomers. In fact this could be a consequence of the use of the asymmetric HAMILTONIAN.

Table 5.3: Comparisons and assignments of fundamentals, overtones and combination bands for $C^{35}Cl_3F$ determined for the PES 'A', 'B', 'C' and 'D' using MM-VCI (MULTIMODE) and SP (SPECTRO) and for $C^{35}Cl_2^{37}ClF$ using PES 'B' (For those frequencies where degeneracy is abolished the average of the A' and A'' assigned values are indicated). All values are given in cm^{-1} . Some of the experimental data are estimated with the help of experimental combinational values.

Assignments $n_1n_2n_3n_4n_5n_6$	$C^{35}Cl_3F$						$C^{35}Cl_2^{37}ClF$		
	$\Gamma_{C_{3v}}^{irr}$	exp. [49]	'A' (MM)	'B' (SP)	'C' (SP)	'D' (MM)	$\Gamma_{C_s}^{irr}$	exp. [49]	'B'
0000 ⁰ 0 ⁰ 0 ⁰	A_1	ZPE	2481.8	2478.8	2479.0	2421.0	A'	ZPE	2472.6
0000 ⁰ 0 ⁰ 1 ¹	E	244.1	243.8	243.5	243.8	238.3	A', A''	242.2	241.6
0010 ⁰ 0 ⁰ 0 ⁰	A_1	351.4	349.6	349.7	349.8	341.7	A'	349.22	347.5
0000 ⁰ 1 ¹ 0 ⁰	E	399.2	398.4	398.4	398.5	392.6	A', A''	395.9	394.6
0000 ⁰ 0 ⁰ 2 ⁰	A_1	-	487.2	487.0	487.5				
0000 ⁰ 0 ⁰ 2 ²	E	-	488.0	487.3	487.8				
0100 ⁰ 0 ⁰ 0 ⁰	A_1	538.2	537.1	537.7	537.7	526.5	A'	535.6	535.2
0010 ⁰ 0 ⁰ 1 ¹	E	-	593.7	593.2	593.6				
000 ⁰ 1 ¹ 1 ¹	E	-	642.5	641.8	642.2				
0020 ⁰ 0 ⁰ 0 ⁰	A_1	-	699.0	699.3	699.4				
0010 ⁰ 1 ¹ 0 ⁰	E	-	747.7	747.7	747.9				
0100 ⁰ 0 ⁰ 1 ¹	E	781.7	780.4	780.6	780.9		A''	777.2	776.3
0000 ⁰ 2 ⁰ 0 ⁰	A_1	-	796.1	795.9	796.1				
0000 ⁰ 2 ² 0 ⁰	E	-	795.8	795.8	795.9				
0001 ¹ 0 ⁰ 0 ⁰	E	849.5	827.6	827.3	827.9	812.1	A', A''	848.9	826.5
0110 ⁰ 0 ⁰ 0 ⁰	A_1	888.7	886.0	886.6	886.7		A'	884.0	881.9
0100 ⁰ 1 ¹ 0 ⁰	E	936.5	936.0	936.9	936.9				
0001 ¹ 0 ⁰ 1 ¹	A_2	-	1070.2	1069.3	1069.2				
	E	-	1070.9	1069.7	1069.9				
0200 ⁰ 0 ⁰ 0 ⁰	A_1	-	1072.8	1074.2	1074.2				
1000 ⁰ 0 ⁰ 0 ⁰	A_1	1081.9	1092.3	1093.1	1093.3	1065.4	A'	1080.7	1093.0
0110 ⁰ 0 ⁰ 1 ¹	E	1132.2	1130.4	-	-				
0011 ¹ 0 ⁰ 0 ⁰	E	-	1175.8	1175.2	1175.1				
0001 ¹ 1 ¹ 0 ⁰	A_1	-	1225.7	1223.4	1222.4				
	A_2	-	1228.5	1224.0	1225.5				
	E	-	1224.0	1223.6	1224.0				
1000 ⁰ 0 ⁰ 1 ¹	E	1324.2	1337.2	1337.1	1335.4				
0101 ¹ 0 ⁰ 0 ⁰	E	-	1361.6	1361.8	1361.4				
1010 ⁰ 0 ⁰ 0 ⁰	A_1	-	1442.9	1443.8	1442.1				
1000 ⁰ 1 ¹ 0 ⁰	E	-	1487.9	1488.0	1486.9				
1100 ⁰ 0 ⁰ 0 ⁰	A_1	-	1628.0	1629.4	1628.2				
0002 ⁰ 0 ⁰ 0 ⁰	A_1	-	1644.8	1647.9	1646.7				
0002 ² 0 ⁰ 0 ⁰	E	-	1653.8	1653.2	1650.7				
1001 ¹ 0 ⁰ 0 ⁰	E	-	1920.2	1921.0	1918.2				
2000 ⁰ 0 ⁰ 0 ⁰	A_1	2145.2	2174.4	2168.8	2165.8				

Table 5.4: Rotational constants B_e^α and corresponding experimental values [52, 4] in cm^{-1} determined for all isotopomers with the help of PES 'B' and for $\text{C}^{35}\text{Cl}_3\text{F}$ also with 'C'

Isotopomer	A	exp.	B	exp.	C	exp.
'C': $\text{C}^{35}\text{Cl}_3\text{F}$	0.0820	-	0.0820	0.08225098	0.0574	0.05771
'B': $\text{C}^{35}\text{Cl}_3\text{F}$	0.0820	-	0.0820	0.08225098	0.0574	0.05771
$\text{C}^{35}\text{Cl}_2^{37}\text{ClF}$	0.0819	0.082160	0.0798	0.080036	0.0563	0.056606
$\text{C}^{35}\text{Cl}^{37}\text{Cl}_2\text{F}$	0.0808	0.081034	0.07868	0.078898	0.05529	0.055608
$\text{C}^{37}\text{Cl}_3\text{F}$	0.07861	-	0.07861	-	0.05428	-

Table 5.5: Comparison of experimental and calculated intensities \mathcal{G}_i [pm^2] for the fundamentals (within the double harmonic approximation) of CCl_3F . The indices i correspond to the energetical order of the fundamentals. See also table 5.6.

i	\mathcal{G}_i^{obs} exp. [7]	\mathcal{G}_i^{eff} 'B'
1	2.61 ± 0.22	2.67
4	0.0346 ± 0.0012	0.0551
7	0.0137 ± 0.0024	0.007
2/3	7.40 ± 0.59	8.2
5/6	0.00206 ± 0.00041	0.0068
8/9	≤ 0.0007	0.0022

Discussing rotational constants in table 5.4

Table 5.4 shows the coherent influence of the isotopic shift on the results for rotational constants. A and B - which have to be identical in the case of the C_{3v} symmetric isotopomers - agree completely despite the use of the asymmetric HAMILTONIAN. A likewise excellent agreement with experiment is to be noted.

Discussing absorption intensities in table 5.5

All absorption intensities show very good results in comparison to experiment. Except for the "problematic" $\mathcal{G}_{2/3}^{eff}$ are all deviations from experiment smaller than 0.05 pm^2 . As already explained in chapter 4.3.1 the corrections for the temperature dependency of the absorption improved the values in comparison to experiment especially for the low lying degenerate fundamentals. The ν_{89} band has an intensity which is below the minimum detectable signal. The intensities do not differ by more than 0.002 pm^2 for the individual isotopomers.

Table 5.6: Harmonic frequencies ω_i in cm^{-1} calculated by SPECTRO for all isotopomers

i	$\text{C}^{35}\text{Cl}_3\text{F}$	$\text{C}^{37}\text{Cl}_3\text{F}$	$\text{C}^{35}\text{Cl}_2^{37}\text{ClF}$	$\text{C}^{35}\text{Cl}^{37}\text{Cl}_2\text{F}$
1	1113.300	1113.292	1113.292	1113.292
2	839.387	839.297	839.261	839.297
3	839.339	838.104	838.140	838.104
4	542.978	540.411	540.411	540.411
5	402.182	401.903	401.884	401.903
6	402.156	398.379	398.398	398.379
7	351.970	349.720	349.720	349.720
8	245.328	244.063	244.065	244.063
9	245.327	242.899	242.898	242.899

Discussing anharmonic constants in table 5.7 and 5.8

The order of the vibrational levels in table 5.7 and 5.8 corresponds to the l-matrix presented in chapter 3.4 or to the table 5.6 above.

The agreement with experiment is very good for nearly all values which can be compared. Nevertheless x_{18} and x_{19} deviate considerably from experiment. This is an exception since all other experimental values are very well reproduced. It might be because it involves the normal mode ν_1 which shows an unexpected isotopic shift (see below) and which deviates by $\sim 10 \text{ cm}^{-1}$ from experiment.

The experimental values had been determined by a Birge-Sponer analysis of the measured spectrum which takes into account fundamentals, overtones, combination bands and hot band transitions. If an analysis of only the corresponding fundamentals and their combination is carried out the experimental value would reduce in magnitude to $\approx -1.2 \text{ cm}^{-1}$.

Considering in table 5.7 those anharmonic constants which do depend on symmetry ($x_{tt'}$) it becomes evident that the difference in anharmonicity due to symmetry is small. This might be a further reason why it is not astonishing that the other calculated results for the vibrational levels for symmetric and asymmetric isotopomers using the asymmetric HAMILTONIAN are quite similar.

As it could already be seen in the eigenvalue spectrum the isotopic shift has already for the anharmonic constants the correct tendency. Again only the results for CCl_3F have a deviating behaviour. We find thus consistency with respect to table 5.3. Clearly an isotopic shift can not be seen within the x_{11} . The corresponding normal mode ν_1 corresponds to a C-F stretching while a systematic decrease in anharmonicity is observed. This might reflect the error which has been already observed for the fundamental ν_1 with respect to experiment. Surprisingly, when considering

the x_{2i} or x_{3i} , degenerate C-Cl stretching normal modes ν_2 and ν_3 having even a larger error than ν_1 show as an isotopic shift a systematic decrease in anharmonicity. This might be due to compensating errors.

From the results for those anharmonic constants of symmetric top isotopomers which have to be identical (x_{sta} and x_{stb} or x_{ata} and x_{atb}) it becomes clear that the order of numerical inaccuracies is in the range of less than 0.1 cm^{-1} . Furthermore one can see in table 5.7 that the results for the anharmonic constants which stem from the Coupling Approach PES ('C') are often slightly closer to the experimental values than those stemming from PES 'B'.

In table 5.8 all results for the degenerate/degenerate anharmonic constants seen by different symmetries are displayed. From this table it is obvious that the two ways of transforming the x^{asym} to x^{sym} leads to significantly different values.

Both ways of transformation involve approximations. One by directly correlating quantum numbers of an asymmetric top representation with quantum numbers of a symmetric top expression. The other by simply averaging vibrational levels. However, the latter allows in a way to determine an error since the deviation of the mean value from the original eigenvalues is known. The error of the anharmonic constants x ranges in the order of a few percent with the exception of Δx_{28} ($\approx 100 \text{ C}^{37}\text{Cl}_3\text{F}$ involving the degenerate normal mode 8 for which already the fundamental has been the most difficult to predict in comparison to experiment. In general the errors for $\text{C}^{37}\text{Cl}_3\text{F}$ are larger than for $\text{C}^{35}\text{Cl}_3\text{F}$. The errors for the g constants often range in the order of 100. Even though large errors are observed for the 'SPEC' results table 5.8 clearly demonstrates that the 'HAMDIF' method does not yield anharmonic constants which correspond to their eigenvalue spectrum. This can easily be shown by recalculating an "eigenvalue spectrum^{sym}" again by using the obtained x_{HAMDIF}^{sym} and x_{SPEC}^{sym} and comparing it to the SPECTRO "eigenvalue spectrum^{asym}". It is trivial that the results for those eigenvalues which have been used to determine x_{SPEC}^{sym} will be better reproduced by using x_{SPEC}^{sym} . But what about the combination bands? As an example will be considered the state $(\nu_4 + \nu_8)$ of $\text{C}^{37}\text{Cl}_3\text{F}$. Its energy indicated in the SPECTRO "eigenvalue spectrum^{asym}" is $776.57215 \text{ cm}^{-1}$. Trying to recalculate this with the help of the x^{sym} shown in table 5.7 and 5.8 we find:

$$\begin{aligned}
 (\nu_4 + \nu_8) &= \nu_4 + \nu_8 + x_{44}^{sym} + x_{48}^{sym} + x_{88}^{sym} + g_{88}^{sym} \\
 &= 398.19 \text{ cm}^{-1} + 241.79 \text{ cm}^{-1} - 0.599 \text{ cm}^{-1} + 0.81 \text{ cm}^{-1} \\
 &\quad + x_{88}^{sym} + g_{88}^{sym} \\
 &= 777.39 \text{ cm}^{-1} + x_{88}^{sym} + g_{88}^{sym}
 \end{aligned}$$

Table 5.7: Anharmonic constants x_{ij}^{asym} and their experimental values [49] in $[\text{cm}^{-1}]$ determined for all isotopomers with the help of PES 'B' and for $\text{C}^{35}\text{Cl}_3\text{F}$ in addition with the help of PES 'C'. All experimental values refer to a symmetric top system even for the asymmetric top isotopomers. There is neither experimental evidence for $\text{C}^{37}\text{Cl}_3\text{F}$ nor for any degenerate/degenerate anharmonicity tt' . The order of the vibrational level corresponds to the energetical order (see table 5.6). All anharmonic constants are given within the asymmetric top description being copied from the SPECTRO output.

ij	$(\text{C}^{35}\text{Cl}_3\text{F})$			$\text{C}^{37}\text{Cl}_3\text{F}$	$\text{C}^{35}\text{Cl}_2^{37}\text{ClF}$		$\text{C}^{35}\text{Cl}^{37}\text{Cl}_2\text{F}$	
	x_{ij} ('C')	x_{ij} ('B')	exp.	x_{ij}	x_{ij}	exp.	x_{ij}	exp.
11	-8.764	-8.701	-9,17(5)	-8.697	-8.702	-9.08	-8.700	-9.00(2)
12	0.066	0.426	-	0.353	0.367	-	0.408	-
13	0.108	0.425	-	0.301	0.347	-	0.367	-
14	-1.166	-1.420	-	-1.473	-1.461	-	-1.464	-
15	-3.223	-3.458	-	-3.426	-3.484	-	-3.457	-
16	-3.211	-3.460	-	-3.423	-3.420	-	-3.412	-
17	0.681	0.977	-	1.022	0.989	-	1.008	-
18	0.546	0.473	-3.65	0.484	0.445	-3.65	0.471	-
19	0.552	0.477	-3.65	0.437	0.425	-3.65	0.473	-
22	-3.323	-3.466	-	-3.392	-3.515	-	-3.497	-
23	-1.520	-1.369	-	-1.333	-1.387	-	-1.105	-
24	-3.343	-3.013	-	-2.873	-3.147	-	-3.061	-
25	-1.979	-1.816	-	-1.753	-2.186	-	-1.971	-
26	0.354	0.382	-	0.326	0.287	-	0.213	-
27	-1.634	-1.762	-	-1.696	-1.794	-	-1.801	-
28	-1.244	-1.243	-	-1.1475	-1.579	-1.579	-1.615	-
29	-1.350	-1.654	-	-1.616	-1.275	-	-1.221	-
33	-2.942	-3.508	-	-3.431	-3.419	-	-3.490	-
34	-3.337	-3.014	-	-2.925	-2.933	-	-2.892	-
35	0.355	0.293	-	0.287	0.392	-	0.281	-
36	-1.929	-2.045	-	-2.074	-1.954	-	-1.876	-
37	-1.683	-1.756	-	-1.699	-1.681	-	-1.662	-
38	-1.417	-1.640	-	-1.622	-1.237	-	-1.230	-
39	-1.224	-1.357	-	-1.248	-1.601	-	-1.574	-
44	-0.592	-0.621	-	-0.599	-0.612	-	-0.604	-
45	0.753	0.761	1.06	0.800	0.805	-	0.792	-
46	0.764	0.751	1.06	0.818	0.832	-	0.836	-
47	-0.691	-0.833	-0.87	-0.768	-0.807	-0.82	-0.786	-
48	-0.617	-0.643	-0.59	-0.5915	-0.639	-0.57	-0.629	-0.55
49	-0.603	-0.624	-0.59	-0.603	-0.600	-0.57	-0.608	-0.55
55	-0.449	-0.435	-	-0.433	-0.406	-	-0.387	-
56	-0.967	-0.882	-	-0.815	-0.786	-	-0.827	-
57	-0.373	-0.359	-	-0.377	-0.333	-	-0.328	-
58	-0.294	-0.387	-	-0.295	-0.024	-	0.027	-
59	0.044	-0.012	-	-0.095	-0.312	-	-0.345	-
66	-0.428	-0.401	-	-0.366	-0.420	-	-0.393	-
67	-0.373	-0.356	-	-0.371	-0.385	-	-0.398	-
68	0.014	-0.008	-	-0.084	-0.364	-	-0.371	-
69	-0.276	-0.309	-	-0.216	-0.030	-	0.016	-
77	-0.079	-0.077	-	-0.079	-0.077	-	-0.077	-
78	-0.007	-0.052	-	-0.047	-0.066	-	-0.065	-
79	-0.007	-0.073	-	-0.078	-0.067	-	-0.042	-
88	-0.051	-0.060	-	-0.049	-0.058	-	-0.050	-
89	0.205	0.199	-	0.190	0.192	-	0.212	-
99	-0.044	-0.053	-	-0.043	-0.049	-	-0.044	-

$$\begin{aligned}
(\nu_4 + \nu_8)'_{HAMDIFF'} &= 777.39 \text{ cm}^{-1} + (x_{88}^{sym})'_{HAMDIFF'} + (g_{88}^{sym})'_{HAMDIFF'} \\
&= 777.39 \text{ cm}^{-1} - 0.05 \text{ cm}^{-1} + 0.14 \text{ cm}^{-1} = 777.49 \text{ cm}^{-1}
\end{aligned}$$

while for 'SPEC'

$$\begin{aligned}
(\nu_4 + \nu_8)'_{SPEC'} &= 777.39 \text{ cm}^{-1} + (x_{88}^{sym})'_{SPEC'} + (g_{88}^{sym})'_{SPEC'} \\
&= 777.39 \text{ cm}^{-1} - 1.27 \text{ cm}^{-1} + 0.48 \text{ cm}^{-1} = 776.6 \text{ cm}^{-1}
\end{aligned}$$

Other combination bands in the "eigenvalue spectrum^{asym}" are nicely reproduced by both $x_{HAMDIFF'}^{sym}$ and $x_{SPEC'}^{sym}$.

Unfortunately, experimental evidence is very poor for all isotopomers and it is thus not clear how good the results are. However, a first rough estimate is certainly given by $x_{SPEC'}^{sym}$.

Table 5.8: Anharmonic constants $x_{tt'}$ and $g_{tt'}$ in $[\text{cm}^{-1}]$ determined for all symmetric top isotopomers within the asymmetric top description and the symmetric top description. Values in column 'HAMDIF' are obtained by subtracting the two HAMILTONIANS as described in Appendix A. Values in column 'SPEC' are obtained by calculating them from the asymmetric top eigenvalue spectrum. For the latter an estimated error is given which is determined according to chapter 4.3.1. by the means of deviation from the SPECTRO output values. The order of the vibrational level corresponds to the energetical order (see table 5.6).

tt'	$\text{C}^{35}\text{Cl}_3\text{F}$				$\text{C}^{37}\text{Cl}_3\text{F } x^{asym}$			
	x^{asym}	$x_{HAMDIF'}^{sym}$	$x_{SPEC'}^{sym}$	$\pm \text{error}$	x^{asym}	$x_{HAMDIF'}^{sym}$	$x_{SPEC'}^{sym}$	$\pm \text{error}$
22	-3.466	-3.487	-3.678	0.17	-3.392	-3.411	-4.203	0.75
23	-1.369	-	-		-1.333	-	-	
25	-1.816	-0.797	-2.211	0.08	-1.753	-0.803	-2.291	0.75
26	0.382	-	-		0.326	-	-	
28	-1.243	-1.474	-1.803	0.08	-1.175	-1.415	-0.718	0.675
29	-1.654	-	-		-1.616	-	-	
33	-3.508	-	-		-3.431	-	-	
35	0.293	-	-		0.287	-	-	
36	-2.045	-	-		-2.074	-	-	
38	-1.640	-	-		-1.622	-	-	
39	-1.357	-	-		-1.248	-	-	
55	-0.435	-0.418	-0.397	0.005	-0.433	-0.399	1.302	0.75
56	-0.882	-	-		-0.815	-	-	
58	-0.387	-0.179	0.001	0.01	-0.295	-0.172	-0.230	0.675
59	-0.012	-	-		-0.095	-	-	
66	-0.401	-	-		-0.366	-	-	
68	-0.008	-	-		-0.084	-	-	
69	-0.309	-	-		-0.216	-	-	
88	-0.060	-0.057	-0.059	0.005	-0.049	-0.046	-1.268	0.6
89	0.199	-	-		0.190	-	-	
99	-0.053	-	-		-0.043	-	-	
g_{22}	-	2.765	0.748	0.65	-	2.745	1.280	0.6
g_{25}	-	-1.239	1.446	1.8	-	-1.110	4.640	0.7
g_{28}	-	0.465	0.290	0.02	-	0.204	-0.772	0.4
g_{55}	-	0.149	-0.022	0.0006	-	-0.008	-1.277	0.4
g_{58}	-	-0.162	-0.169	0.125	-	-0.083	2.768	0.5
g_{88}	-	0.145	0.041	0.04	-	0.141	0.476	0.1

5.2 Conclusions

In this work DFT is used to predict spectroscopic data for CCl_3F . The following new aspects which have been presented are highlighted.

- The hybrid functional PBE0 gives excellent predictions for the most abundant isotopomers of CCl_3F . Simple GGA functionals such as BLYP are inadequate (even LDA gives better results). Simple inspection of geometry optimization calculations facilitates the choice of an appropriate functional for CCl_3F . Concerning the prediction of the C-Cl bond length PBE0 could still be improved.
- DFT allows to determine a PES through terms which involve 3D cuts. 19 single point calculations are sufficient for an analysis using second-order perturbation theory (SPECTRO).
- More interestingly using gradient and second derivative data to determine a PES for normal modes with higher anharmonicity constants only 144 geometries are necessary to be calculated (Coupling Approach + MULTIMODE).
- The vibrational energy levels are determined by variational theory and by perturbation theory. Although perturbation theory gives not the exact eigenvalues, here it yields high quality predictions for the energy levels, which are of the same accuracy as the results obtained by variational calculations. Therefore the optimum would be to proceed in analogy to the generation of PES 'C' and its results. The use of MULTIMODE is recommended because it allows to check easily and cheaply the results. Thus the advantages of these both programs can be joined and exploited extensively
- In this work the use of an asymmetric HAMILTONIAN for the C_{3v} molecules $\text{C}^{35}\text{Cl}_3\text{F}$ and $\text{C}^{37}\text{Cl}_3\text{F}$ is legitimate for the eigenvalue spectrum but not for the anharmonic constants.
- An explicit expression for $g_{tt'}$ in terms of x^{asym} is identified. The expressions to transform anharmonic constants obtained by an asymmetric top HAMILTONIAN into anharmonic constants corresponding to a symmetric top HAMILTONIAN can be calculated by a short FORTRAN program which uses the SPECTRO output as input. Checking the results with the help of the eigenvalue spectrum leads to doubts concerning these results. Eventually, the results for other molecules whose anharmonic constants had already been calculated using the same expressions have to be corrected.
- Including higher dimensional cuts into the PES calculated by cheaper basis sets as DZP does not necessarily improve the results.

- Throughout this study the magnitudes related to normal modes 1 and 2/3 show to be more difficult to predict than magnitudes related to other normal modes. Clearly it would be worth it to undertake efforts in order to increase the accuracy of predictions for these three normal modes.

The Algorithm

As a general conclusion from this work the following algorithm for the calculation of the infrared spectrum of a given molecule is proposed. It follows in principle the procedure used to obtain the results for PES 'C'. This algorithm scales only with N in the calculation time (N being the number of nuclei in the molecule).

The Algorithm

1. Determination of the appropriate functional for the system by comparison of calculated geometries with experiment.
2. DFT calculation of the energies and gradients at $n * (3N - 6)$ points. $n = 16$ was sufficient in the case of CCl_3F .
3. Use the Coupling Approach to obtain the PES (see chapter 2.4) for

$$V(\mathbf{Q}) = \sum_i V(Q_i)^{(1)\text{energies}} + \sum_{j \neq i} V(Q_i, Q_j)^{(2)\text{gradients}}$$

4. Use MM-VCI for the vibrational levels (see chapter 2.2). Results correspond to those for PES 'A'.
5. Calculate all anharmonic constants from the eigenvalue spectrum if and only if the molecule has a symmetry higher than C_s .
6. Derive the force field from the PES.
7. Use it for SPECTRO in order to determine vibrational absorption intensities, rotational constants and, in the case that the molecule has not a symmetry higher than C_s , also anharmonic constants.

5.3 Outlook

All methods used in this work yielded results which are of the state of the art and which come often close to experimental accuracy. However, theoretically there is no limit of improvement until experimental accuracy is reached.

In order to improve for example the reproduction of the two highest lying fundamentals and other properties of the molecule which involve the same normal modes one could make efforts in finding an even more suitable functional for CCl_3F . Alternatively one could increase the number of calculated points on the PES involving their normal modes.

5.3.1 The Coupling Approach for other Molecules

First of all, the other isotopomers of trichlorofluoromethane should be calculated with the same approximations and compared one to each other. If the Coupling Approach likewise shows to yield as excellent results as in this work, larger molecular systems with more anharmonicity are to be tackled trying to keep the error with respect to experiment in the range of errors of the systems considered in this work.

5.3.2 Further development of the grid for the PES within the Coupling Approach

The PES is obtained by using the information of points lying exclusively equidistantly on a 1D grid. This equidistant distribution might introduce numerically bigger errors in regions of the PES where the gradient varies more than in regions where the PES is relatively flat. Thus, it is proposed to distribute in an equidistant manner only a part of the total number (n) of points on the 1D cuts which are to be calculated and then to calculate first their gradients and second derivatives in order to determine rather qualitatively how the gradient varies. If the absolute value of the second derivative is large the number of additional points close to that point for which the second derivative has been calculated should be increased while in those regions where the second derivative is small no more points have to be added.

Furthermore it is proposed to distribute those points being economized by the non-equidistant distribution selectively in regions of the full dimensional PES which are assumed to have large gradients. These regions can be identified by a thorough comparison between the normal modes with respect to the potential energies, the gradients and the second derivatives. Do they differ a lot it is of big interest to calculate further geometries lying in between the normal modes. For example, if $f_{ijj}(Q_{i,m})$ (the second derivative of the potential energy with respect to j at the geometry m of the normal mode i) is a value which is considerably different from

$f_{jii}(Q_{j,m'})$ it is proposed to carry out a single point calculation of the geometry lying between $Q_{i,m}$ and $Q_{j,m'} : Q_{mm'}^{(ij)}$. In other words, if $\Delta_{ff} = |f_{jii}(Q_{j,m'})| - |f_{ijj}(Q_{i,m})|$ is big one should do another calculation at $Q_{mm'}^{(ij)}$. Of course, the closer the values m and m' are the more important the information, therefore a normalization factor for Δ_{ff} is proposed: $\frac{1}{|m-m'|}$. There are Δ for potential energies, gradients and second derivatives at all already calculated geometries on the 1D cuts. One would have to rank them while taking into account that certain combinations might be of special interest. For example, of big interest would be the combination of a big Δ for the potential energy together with gradients where the sign of the energetically lower lying gradient is negative with respect to the mode with the higher potential energy and where the sign of the energetically higher lying gradient is positive with respect to the mode with the lower potential energy. The additional single point calculations can easily be included into the expression for the potential energy within the Coupling Approach by fitting the results in linear combinations of polynomial expansions of the corresponding normal modes. Thus, interpolation enters inherently the Coupling Approach. This improvement can be tested continuously for convergence.

As a testing case the normal modes 1 and 2/3 could be of special interest. Using this study and trying to improve the PES 'mode selectively' for normal mode 1,2 and 3 one could easily quantify any slight improvement.

5.3.3 Further development of SPECTRO

The not working subroutine in SPECTRO which uses an appropriate HAMILTONIAN for symmetric top molecules could be made to work also for orders of the principle rotational axis greater than two. Or a procedure is implemented which determines the anharmonic constants of the symmetric top HAMILTONIAN with the help of the force constants which were estimated within the asymmetric top HAMILTONIAN. Thus one could calculate the same molecule in order to determine quantitatively the influence of using the HAMILTONIAN with the unsuitable symmetry.

Alternatively a small program could be developed which determines the anharmonic constants from the eigenvalue spectrum as it was done in this study within the 'SPEC' approach. Also higher vibrational levels should be calculated for the two HAMILTONIAN.

In addition one should implement routines which can make use of the PES obtained by the Coupling Approach such as 'C'. The values predicted with the help of 'C' were the most precise ones. Therefore any developments in this direction seem to be promising.

Concerning the anharmonic constants it would also be useful to have more experi-

mental evidence in order to compare. Especially further results for x_{18} (see chapter 5.1) and the g constants would be interesting.

Appendix A

Transforming Anharmonic Constants

As already mentioned in chapter 2.2.2 and 3.5 in this appendix some simple relations between the anharmonic constants of the asymmetric top and the symmetric top description are derived.

In order to read in the SPECTRO output for the anharmonic constants x^{asym} and to transform them into x^{sym} and g a small FORTRAN program has been written. The program respects the SPECTRO notation: 1,4 and 7 are non degenerate modes. 2 and 3, 5 and 6, 8 and 9 are the two components a and b of a given degenerate mode. The energy of the modes is decreasing from 1 to 9. The matrix of the anharmonic constants of $C^{35}Cl_3F$ is symmetric with respect to its diagonal and looks like this:

	1	2	3	4	5	6	7	8	9
1	-8.701								
2	0.426	-3.466							
3	0.425	-1.369	-3.508						
4	-1.420	-3.013	-3.014	-0.621					
5	-3.458	-1.816	0.293	0.761	-0.435				
6	-3.460	0.382	-2.045	0.751	-0.882	-0.401			
7	0.977	-1.762	-1.756	-0.833	-0.359	-0.356	-0.077		
8	0.473	-1.243	-1.640	-0.643	-0.387	-0.008	-0.052	-0.060	
9	0.477	-1.654	-1.357	-0.624	-0.012	-0.309	-0.073	0.199	-0.053

Thus, there are $\frac{n \times n}{2} + \frac{n}{2} = 45$ elements. The 6×6 matrix for the anharmonic constants of the symmetric top description contains only 21 elements. In order to

account for numerical inaccuracies all expressions yielding the same element in the 6×6 matrix are averaged by the program. The input for the program has to be an ASCII file named 'input' which contains only the above matrix in the following form:

```

-8.701
0.426  -3.466
0.425  -1.369  -3.508
-1.420  -3.013  -3.014  -0.621
-3.458  -1.816   0.293   0.761  -0.435
-3.460   0.382  -2.045   0.751  -0.882  -0.401
0.977  -1.762  -1.756  -0.833  -0.359  -0.356  -0.077
0.473  -1.243  -1.640  -0.643  -0.387  -0.008  -0.052  -0.060
0.477  -1.654  -1.357  -0.624  -0.012  -0.309  -0.073   0.199  -0.053

```

To read in the input correctly it is important that all elements stand precisely in their column and that the distance between the columns is exactly 6 blanks. The precision of the program's output is adjusted to the precision of the input. So, in the case of bigger anharmonicities than above the output format would have to be adopted. The output of the above input will be in the file 'xsym' which is generated

by the executable and will look like this:

j	i	$xsfin(i, j)$	$gfin(i, j)$
1	1	-8.70100	0.00000
1	2	0.42550	0.00000
1	3	0.00000	0.00000
1	4	-1.42000	0.00000
1	5	-3.45900	0.00000
1	6	0.00000	0.00000
1	7	0.97700	0.00000
1	8	0.47500	0.00000
1	9	0.00000	0.00000
2	2	-3.48700	2.80250
2	3	0.00000	0.00000
2	4	-3.01350	0.00000
2	5	-0.79650	-1.13400
2	6	0.00000	0.00000
2	7	-1.75900	0.00000
2	8	-1.47350	0.17350
2	9	0.00000	0.00000
3	3	0.00000	0.00000
3	4	0.00000	0.00000
3	5	0.00000	0.00000
3	6	0.00000	0.00000
3	7	0.00000	0.00000
3	8	0.00000	0.00000
3	9	0.00000	0.00000
4	4	-0.62100	0.00000
4	5	0.75600	0.00000
4	6	0.00000	0.00000
4	7	-0.83300	0.00000
4	8	-0.63350	0.00000
4	9	0.00000	0.00000
4	5	-0.41800	-0.02300
5	6	0.00000	0.00000
5	7	-0.35750	0.00000
5	8	-0.17900	-0.16900
5	9	0.00000	0.00000
6	6	0.00000	0.00000
6	7	0.00000	0.00000
6	8	0.00000	0.00000
6	9	0.00000	0.00000
7	7	-0.07700	0.00000
7	8	-0.06250	0.00000
7	9	0.00000	0.00000
8	8	-0.05650	0.15600
8	9	0.00000	0.00000
9	9	0.00000	0.00000

(A.1)

By assigning 1,4 and 7 to s, s' and s'' and 2,5 and 8 to t, t' and t'' respectively one has determined all anharmonic constants within the harmonic top description for a C_{3v} symmetric molecule.

Figure A.1: FORTRAN program to transform the x^{asym} into x^{sym} according to the 'HAMDIFF' approach.

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<pre> program xconv *This program transforms xasij into xsymij for c3v symmetric molecules *where mode 1,4 and 7 correspond to non degenerate bands and mode *23,56 and 89 correspond to the two components of a degenerate *mode within the asymmetric top expression. The energy decreases *going from 1 to 9. s denotes non degenerate modes. ta and tb *correspond to the two components of degenerate mode t. The formulas *are according to Handy, H.C, Willets, A., Spectrochim. Acta A, 53, *1169 (1997) and this diploma thesis. dimension x(0:9,0:9),xsym(0:9,0:9),g(0:9,0:9) dimension xsfin(0:9,0:9),gfin(0:9,0:9) integer i,j,k,l,m,n * *loop to read in open(unit=1,file='input') do 200 i=1,9 0 read(1,100) x(i,1),x(i,2),x(i,3),x(i,4),x(i,5),x(i,6),x(i,7), & x(i,8),x(i,9) 100 format(9(F6.3,6X)) * * & in column 6 corresponds to a continuation of the line before * starting with 0 in the 6th column * 0 print*,x(i,1),x(i,2),x(i,3),x(i,4),x(i,5),x(i,6),x(i,7),x(i,8) * & ,x(i,9) 200 continue close(1) * *loop to transform the constants into xsym do 210 j=1,9 do 205 i=j,9 open(unit=2,file='output') 201 format(A,11,11,1X,F8.5) * * this will calculate xsymtt and gtt *for all tata 0 if((i.eq.j).and.((i.eq.2).or.(i.eq.5). & or.(i.eq.8)))then k=i+1 xsym(i,j)=x(i,j) *xsymtt=xasymtata g(i,j)=x(i,j)+0.5*x(k,j) *gtt=1/2xasymtatab-xasymtata write(2,201) 'xsymtata',j,i,xsym(i,j) print*, 'xsymtt',j,i,' = ',xsym(i,j) print*, 'gtt',j,i,' = ',g(i,j) *for all tbtb 0 elseif((i.eq.j).and.((i.eq.3).or.(i.eq.6). & or.(i.eq.9)))then k=j-1 xsym(i,j)=x(i,j) g(i,j)=x(i,j)+0.5*x(i,k) write(2,201) 'xsymtbtb',j,i,xsym(i,j) print*, 'xsymtt',j,i,' = ',xsym(i,j) print*, 'gtt',j,i,' = ',g(i,j) endif * * this will calculate xsymss 0 if(i.ge.j.and.((i.eq.1.or.i.eq.4.or.i.eq.7).and. & (j.eq.1.or.j.eq.4.or.j.eq.7)))then xsym(i,j)=x(i,j) write(2,201) 'xsymss',j,i,xsym(i,j) print*, 'xsymss',j,i,' = ',xsym(i,j) * * this will calculate gtt' and xsymtt' *for all tata' 0 elseif((i.gt.j).and.((i.eq.2).or.(i.eq.5) </pre>		

Figure A.2: program continued

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<pre> & .or. (i.eq.8)).and. ((j.eq.2).or.(j.eq.5).or.(j.eq.8))) then k=i+1 g(i,j)=0.5*x(i,j)-0.5*x(k,j) * print*, 'ggtt\'', j, i, ' = ', g(i,j) xsym(i,j)=0.5*(x(i,j)+x(k,j)) * print*, 'xsymtt\'', j, i, ' = ', xsym(i,j) write(2,201) 'xsymtata\'', j, i, xsym(i,j) *for all tbtb' 0 elseif((i.gt.j).and.(((i.eq.3).or.(i.eq.6).or.(i.eq.9)) & .and. ((j.eq.3).or.(j.eq.6).or.(j.eq.9)))) then k=i-1 g(i,j)=0.5*x(i,j)-0.5*x(k,j) * print*, 'ggtt\'', j, i, ' = ', g(i,j) xsym(i,j)=0.5*(x(i,j)+x(k,j)) write(2,201) 'xsymtbtb\'', j, i, xsym(i,j) * print*, 'xsymtt\'', j, i, ' = ', xsym(i,j) endif * * this will calculate xsymst *for all vertical xst *for all sta 0 if(((j.eq.1).and. & ((i.eq.2).or.(i.eq.5).or.(i.eq.8))).or. ((j.eq.4) & .and. ((i.eq.5).or.(i.eq.8))).or. ((j.eq.7) & .and. (i.eq.8))) then k=i+1 xsym(i,j)=0.5*(x(i,j)+x(k,j)) write(2,201) 'xsymsta', j, i, xsym(i,j) *for all stb 0 elseif(((j.eq.1).and. & ((i.eq.3).or.(i.eq.6).or.(i.eq.9))).or. ((j.eq.4) & .and. ((i.eq.6).or.(i.eq.9))).or. ((j.eq.7) & .and. (i.eq.9))) then k=i-1 xsym(i,j)=0.5*(x(i,j)+x(k,j)) write(2,201) 'xsymstb', j, i, xsym(i,j) * print*, 'xsymst', j, i, ' = ', xsym(i,j) endif * print*, 'xsymst', j, i, ' = ', xsym(5,1) *for all horizontal xst *for all sta 0 if(((i.eq.7).and. & ((j.eq.2).or.(j.eq.5))).or. ((i.eq.4) & .and. (j.eq.2))) then k=j+1 xsym(i,j)=0.5*(x(i,j)+x(i,k)) write(2,201) 'xsymsta', j, i, xsym(i,j) * print*, 'xsymst', j, i, ' = ', xsym(i,j) *for all stb 0 elseif(((i.eq.7).and. & ((j.eq.3).or.(j.eq.6))).or. ((i.eq.4) & .and. (j.eq.3))) then k=j-1 xsym(i,j)=0.5*(x(i,j)+x(i,k)) write(2,201) 'xsymstb', j, i, xsym(i,j) * print*, 'xsymst', j, i, ' = ', xsym(i,j) endif 205 continue 210 continue close(2) * *loop to write input into readinputfile open(unit=3, file='readinput') do 300 j=1,9 do 250 i=j,9 write(3,220) j,i,x(i,j) </pre>		

Figure A.3: program continued

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<pre> 220 format (11,11,F8.4) 250 continue 300 continue close (3) * *loop to write the first transformed constants xsym *and corresponding gtt and gtt' into firstxsym open (unit=4, file='firstxsym') write (4,350) 'j','i','xsym(i,j)','g(i,j)' 350 format (A,1X,A,1X,A,1X,A) do 400 j=1,9 do 390 i=j,9 0 if (((j.ne.2).or.((i.ne.3).and.(i.ne.6).and.(i.ne.9))) & .and.((j.ne.3).or.((i.ne.5).and.(i.ne.8))) & .and.((j.ne.5).or.((i.ne.6).and.(i.ne.9))).and. & ((j.ne.6).or.(i.ne.8)).and.((j.ne.8).or.(i.ne.9)))then * print *,j,i,xsym(i,j) write (4,380) j,i,xsym(i,j),g(i,j) 380 format (11,1X,11,1X,F8.5,1X,F8.5) else xsym(i,j)=0 * print *,j,i,xsym(i,j) write (4,385) j,i,xsym(i,j) 385 format (1X,11,1X,11,F8.5) endif 390 continue 400 continue close (4) * ***** * *loops to transform the xsym into xsfin (averaging the values) * * * this loop will average the xsymtata and gtata with xsymtbtb and * gtbttb, respectively. And it will redefine xsymss in the xsfin * array * for all tt do 405 j=1,9 do 402 i=j,9 0 if ((i.eq.j).and.((i.eq.2).or.(i.eq.5). & or.(i.eq.8)))then k=i+1 l=j+1 xsfin(i,j)=0.5*(xsym(i,j)+xsym(k,l)) gfin(i,j)=0.5*(g(i,j)+g(k,l)) * print *, 'xsymtt',j,i,' = ',xsfin(i,j) * print *, 'gtt',j,i,' = ',gfin(i,j) endif 0 if (i.ge.j.and.((i.eq.1.or.i.eq.4.or.i.eq.7).and. & (j.eq.1.or.j.eq.4.or.j.eq.7)))then xsfin(i,j)=xsym(i,j) * write (2,201) 'xsymss',j,i,xsym(i,j) * print *, 'xsymss',j,i,' = ',xsfin(i,j) endif 402 continue 405 continue * *this will average the gtt' and xsymtt' do 425 j=1,9 do 420 i=j,9 0 if ((i.gt.j).and.((i.eq.2).or.(i.eq.5) & .or.(i.eq.8)).and.((j.eq.2).or.(j.eq.5).or.(j.eq.8))))then k=i+1 l=j+1 gfin(i,j)=0.5*(g(i,j)+g(k,l)) </pre>		

Figure A.4: program continued

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Mar 23, 02 19:43	program	Page 4/4
<pre> xsfin(i,j)=0.5*(xsym(i,j)+xsym(k,l)) * print*, 'gtt\'', j, i, ' - ', gfin(i, j) * print*, 'xsymtt\'', j, i, ' - ', xsfin(i, j) endif 420 continue 425 continue * * this will average the xsymst *for all vertical xst do 435 j=1,9 do 430 i=j,9 if(((j.eq.1).and. & ((i.eq.2).or.(i.eq.5).or.(i.eq.8))).or.((j.eq.4) & .and.((i.eq.5).or.(i.eq.8))).or.((j.eq.7) & .and.(i.eq.8))) then k=i+1 xsfin(i,j)=0.5*(xsym(i,j)+xsym(k,j)) * print*, 'xsymst', j, i, ' - ', xsfin(i, j) endif 430 continue 435 continue *for all horizontal xst do 450 j=1,9 do 445 i=j,9 if(((i.eq.7).and. & ((j.eq.2).or.(j.eq.5))).or.((i.eq.4) & .and.(j.eq.2))) then k=j+1 xsfin(i,j)=0.5*(xsym(i,j)+xsym(i,k)) * print*, 'xsymst', j, i, ' - ', xsfin(i, j) endif 445 continue 450 continue * *loop to write the final transformed symmetric constants *and corresponding gtt and gtt' into xsym open(unit=5, file='xsym') write(5,550) 'j', 'i', 'xsfin(i, j)', 'gfin(i, j)' 550 format(A, 1X, A, 1X, A, 1X, A) do 600 j=1,9 do 599 i=j,9 0 if(((i.eq.3).or.(i.eq.6).or.(i.eq.9)).or. & (j.eq.3).or.(j.eq.6).or.(j.eq.9))then xsfin(i,j)=0 print*, j, i, xsfin(i, j) else print*, j, i, xsfin(i, j) endif 0 if((i.eq.j).and.((i.eq.2).or.(i.eq.5). & or.(i.eq.8)))then print*, j, i, gfin(i, j), ' gfin' 0 elseif(((i.eq.2).or.(i.eq.5).or.(i.eq.8)) & .and.((j.eq.2).or.(j.eq.5).or.(j.eq.8)))then print*, j, i, gfin(i, j), ' gfin' else gfin(i, j)=0 print*, j, i, gfin(i, j), ' gfin=0' endif write(5,580) j, i, xsfin(i, j), gfin(i, j) 580 format(1I, 1X, 1I, 1X, F8.5, 1X, F8.5) 599 continue 600 continue close(5) end </pre>		

All MATHEMATICA files which have been used to determine by successive substitution from the SPECTRO output the anharmonic constants within the 'HAMD-IFF' approach are also shown in this appendix. The following indeces have been used (unlike to the previous text):

- Normal modes 1,2 and 3 are defined to be the non degenerate normal modes ${}_{s,s}'$ and ${}_{s,s}''$ (in the previous text 1, 4 and 7).
- Normal modes 4, 5 and 6 are the degenerate normal modes ${}_{t,t'}^{sym,sym}$ and ${}_{t''}^{sym}$ or ${}_{ta,ta'}^{asym,asym}$ and ${}_{ta''}^{asym}$, respectively (in the previous text 2, 5 and 8).
- Normal modes 7,8 and 9 correspond to ${}_{tb,tb'}^{asym,asym}$ and ${}_{tb''}^{asym}$, respectively (in the previous text 3, 6 and 9).
- All quantum numbers n correspond either to n_s^{asym} or account for the symmetric top expression.
- All quantum numbers nas account for the degenerate modes in the asymmetric top expression.
- x is equivalent to x^{sym} , xas to x^{asym} .

The following two correlation have been assumed (according to chapter 3.5 and [50]): $n_t = 1$ and $l_t = 1$ corresponds to $nas_{ta} = 1$ and $nas_{tb} = 0$ while $n_t = 2$ and $l_t = 2$ are correlated with $nas_{ta} = 1$ and $nas_{tb} = 1$. All files which were used to obtain the equations listed in chapter 3.5 are printed out in the following order (each determined variable is incorporated into the determination of the following file):

1. Determination of the difference between the zero point energies (ZPE) for all $n = 0$.

Figure A.5: Determination of the difference between the zero point energies (ZPE).

 dE_{nb}

1

```

omsym = w1 (n1 + 0.5) + w2 (n2 + 0.5) + w3 (n3 + 0.5) + w4 (n4 + 1) + w5 (n5 + 1) + w6 (n6 + 1)

(0.5 + n1) w1 + (0.5 + n2) w2 + (0.5 + n3) w3 + (1 + n4) w4 + (1 + n5) w5 + (1 + n6) w6

xsssym = x11 (n1 + 0.5) ^2 + x22 (n2 + 0.5) ^2 + x33 (n3 + 0.5) ^2 +
x12 (n1 + 0.5) (n2 + 0.5) + x13 (n1 + 0.5) (n3 + 0.5) + x23 (n2 + 0.5) (n3 + 0.5)

(0.5 + n1) ^2 x11 + (0.5 + n1) (0.5 + n2) x12 + (0.5 + n1) (0.5 + n3) x13 +
(0.5 + n2) ^2 x22 + (0.5 + n2) (0.5 + n3) x23 + (0.5 + n3) ^2 x33

xstsym = (n1 + 0.5) (x14 (n4 + 1) + x15 (n5 + 1) + x16 (n6 + 1)) +
(n2 + 0.5) (x24 (n4 + 1) + x25 (n5 + 1) + x26 (n6 + 1)) +
(n3 + 0.5) (x34 (n4 + 1) + x35 (n5 + 1) + x36 (n6 + 1))

General::spell1: Possible spelling error: new symbol name "xstsym" is similar to existing symbol "xsssym".

(0.5 + n1) ((1 + n4) x14 + (1 + n5) x15 + (1 + n6) x16) +
(0.5 + n2) ((1 + n4) x24 + (1 + n5) x25 + (1 + n6) x26) +
(0.5 + n3) ((1 + n4) x34 + (1 + n5) x35 + (1 + n6) x36)

xttsym = x44 (n4 + 1) ^2 + x55 (n5 + 1) ^2 + x66 (n6 + 1) ^2 +
x45 (n4 + 1) (n5 + 1) + x46 (n4 + 1) (n6 + 1) + x56 (n5 + 1) (n6 + 1)

General::spell1: Possible spelling error: new symbol name "xttsym" is similar to existing symbol "xstsym".

(1 + n4) ^2 x44 + (1 + n4) (1 + n5) x45 + (1 + n4) (1 + n6) x46 +
(1 + n5) ^2 x55 + (1 + n5) (1 + n6) x56 + (1 + n6) ^2 x66

gttsym = g44 * 14 ^2 + g55 * 15 ^2 + g66 * 16 ^2 + g45 * 14 * 15 + g46 * 14 * 16 + g56 * 15 * 16

General::spell1: Possible spelling error: new symbol name "gttsym" is similar to existing symbol "xttsym".

g44 14^2 + g45 14 15 + g55 15^2 + g46 14 16 + g56 15 16 + g66 16^2

Esym = omsym + xsssym + xstsym + xttsym + gttsym

g44 14^2 + g45 14 15 + g55 15^2 + g46 14 16 + g56 15 16 + g66 16^2 + (0.5 + n1) w1 + (0.5 + n2) w2 +
(0.5 + n3) w3 + (1 + n4) w4 + (1 + n5) w5 + (1 + n6) w6 + (0.5 + n1) ^2 x11 + (0.5 + n1) (0.5 + n2) x12 +
(0.5 + n1) (0.5 + n3) x13 + (0.5 + n1) ((1 + n4) x14 + (1 + n5) x15 + (1 + n6) x16) + (0.5 + n2) ^2 x22 +
(0.5 + n2) (0.5 + n3) x23 + (0.5 + n2) ((1 + n4) x24 + (1 + n5) x25 + (1 + n6) x26) +
(0.5 + n3) ^2 x33 + (0.5 + n3) ((1 + n4) x34 + (1 + n5) x35 + (1 + n6) x36) + (1 + n4) ^2 x44 +
(1 + n4) (1 + n5) x45 + (1 + n4) (1 + n6) x46 + (1 + n5) ^2 x55 + (1 + n5) (1 + n6) x56 + (1 + n6) ^2 x66

omasym = w1 (n1 + 0.5) + w2 (n2 + 0.5) + w3 (n3 + 0.5) + w4 (nas4 + 0.5) +
w5 (nas5 + 0.5) + w6 (nas6 + 0.5) + w7 (nas7 + 0.5) + w8 (nas8 + 0.5) + w9 (nas9 + 0.5)

General::spell1: Possible spelling error: new symbol name "omasym" is similar to existing symbol "omsym".

(0.5 + n1) w1 + (0.5 + n2) w2 + (0.5 + n3) w3 + (0.5 + nas4) w4 +
(0.5 + nas5) w5 + (0.5 + nas6) w6 + (0.5 + nas7) w7 + (0.5 + nas8) w8 + (0.5 + nas9) w9

xssasym = x11 (n1 + 0.5) ^2 + x22 (n2 + 0.5) ^2 + x33 (n3 + 0.5) ^2 +
x12 (n1 + 0.5) (n2 + 0.5) + x23 (n2 + 0.5) (n3 + 0.5) + x13 (n1 + 0.5) (n3 + 0.5)

General::spell1: Possible spelling error: new symbol name "xssasym" is similar to existing symbol "xsssym".

(0.5 + n1) ^2 x11 + (0.5 + n1) (0.5 + n2) x12 + (0.5 + n1) (0.5 + n3) x13 +
(0.5 + n2) ^2 x22 + (0.5 + n2) (0.5 + n3) x23 + (0.5 + n3) ^2 x33

```

Figure A.6: Determination of the difference between the zero point energies (ZPE) continued.

dE.nb

2

```

xstasym = (n1 + 0.5) (kas14 (nas4 + 0.5) + kas15 (nas5 + 0.5) +
  kas16 (nas6 + 0.5) + kas17 (nas7 + 0.5) + kas18 (nas8 + 0.5) + kas19 (nas9 + 0.5) ) +
  (n2 + 0.5) (kas24 (nas4 + 0.5) + kas25 (nas5 + 0.5) + kas26 (nas6 + 0.5) +
  kas27 (nas7 + 0.5) + kas28 (nas8 + 0.5) + kas29 (nas9 + 0.5) ) +
  (n3 + 0.5) (kas34 (nas4 + 0.5) + kas35 (nas5 + 0.5) + kas36 (nas6 + 0.5) +
  kas37 (nas7 + 0.5) + kas38 (nas8 + 0.5) + kas39 (nas9 + 0.5) )

General::spell1 :
Possible spelling error: new symbol name "xstasym" is similar to existing symbols {kmasym, kstasym}.

(0.5 + n1) ((0.5 + nas4) kas14 + (0.5 + nas5) kas15 +
  (0.5 + nas6) kas16 + (0.5 + nas7) kas17 + (0.5 + nas8) kas18 + (0.5 + nas9) kas19) +
(0.5 + n2) ((0.5 + nas4) kas24 + (0.5 + nas5) kas25 + (0.5 + nas6) kas26 +
  (0.5 + nas7) kas27 + (0.5 + nas8) kas28 + (0.5 + nas9) kas29) +
(0.5 + n3) ((0.5 + nas4) kas34 + (0.5 + nas5) kas35 + (0.5 + nas6) kas36 +
  (0.5 + nas7) kas37 + (0.5 + nas8) kas38 + (0.5 + nas9) kas39)

xttasym = kas44 (nas4 + 0.5) ^2 + kas55 (nas5 + 0.5) ^2 +
  kas66 (nas6 + 0.5) ^2 + kas77 (nas7 + 0.5) ^2 + kas88 (nas8 + 0.5) ^2 +
  kas99 (nas9 + 0.5) ^2 + (nas4 + 0.5) (kas45 (nas5 + 0.5) + kas46 (nas6 + 0.5) +
  kas47 (nas7 + 0.5) + kas48 (nas8 + 0.5) + kas49 (nas9 + 0.5) ) + (nas5 + 0.5)
  (kas56 (nas6 + 0.5) + kas57 (nas7 + 0.5) + kas58 (nas8 + 0.5) + kas59 (nas9 + 0.5) ) +
  (nas6 + 0.5) (kas67 (nas7 + 0.5) + kas68 (nas8 + 0.5) + kas69 (nas9 + 0.5) ) +
  (nas7 + 0.5) (kas78 (nas8 + 0.5) + kas79 (nas9 + 0.5) ) + kas89 (nas8 + 0.5) (nas9 + 0.5)

General::spell1 :
Possible spelling error: new symbol name "xttasym" is similar to existing symbols {kstasym, kttasym}.

(0.5 + nas4) ^2 kas44 +
(0.5 + nas4) ((0.5 + nas5) kas45 + (0.5 + nas6) kas46 + (0.5 + nas7) kas47 + (0.5 + nas8) kas48 +
  (0.5 + nas9) kas49) + (0.5 + nas5) ^2 kas55 +
(0.5 + nas5) ((0.5 + nas6) kas56 + (0.5 + nas7) kas57 + (0.5 + nas8) kas58 + (0.5 + nas9) kas59) +
(0.5 + nas6) ^2 kas66 +
(0.5 + nas6) ((0.5 + nas7) kas67 + (0.5 + nas8) kas68 + (0.5 + nas9) kas69) +
(0.5 + nas7) ^2 kas77 + (0.5 + nas7) ((0.5 + nas8) kas78 + (0.5 + nas9) kas79) +
(0.5 + nas8) ^2 kas88 + (0.5 + nas8) (0.5 + nas9) kas89 + (0.5 + nas9) ^2 kas99

Easym = omasym + kmasym + xstasym + xttasym

General::spell1 : Possible spelling error: new symbol name "Easym" is similar to existing symbol "Esym".

(0.5 + n1) w1 + (0.5 + n2) w2 + (0.5 + n3) w3 + (0.5 + nas4) w4 + (0.5 + nas5) w5 +
  (0.5 + nas6) w6 + (0.5 + nas7) w7 + (0.5 + nas8) w8 + (0.5 + nas9) w9 + (0.5 + n1) ^2 k11 +
  (0.5 + n1) (0.5 + n2) k12 + (0.5 + n1) (0.5 + n3) k13 + (0.5 + n2) ^2 k22 +
  (0.5 + n2) (0.5 + n3) k23 + (0.5 + n3) ^2 k33 + (0.5 + n1) ((0.5 + nas4) kas14 + (0.5 + nas5) kas15 +
  (0.5 + nas6) kas16 + (0.5 + nas7) kas17 + (0.5 + nas8) kas18 + (0.5 + nas9) kas19) +
  (0.5 + n2) ((0.5 + nas4) kas24 + (0.5 + nas5) kas25 + (0.5 + nas6) kas26 +
  (0.5 + nas7) kas27 + (0.5 + nas8) kas28 + (0.5 + nas9) kas29) +
  (0.5 + n3) ((0.5 + nas4) kas34 + (0.5 + nas5) kas35 + (0.5 + nas6) kas36 +
  (0.5 + nas7) kas37 + (0.5 + nas8) kas38 + (0.5 + nas9) kas39) + (0.5 + nas4) ^2 kas44 +
  (0.5 + nas4) ((0.5 + nas5) kas45 + (0.5 + nas6) kas46 + (0.5 + nas7) kas47 +
  (0.5 + nas8) kas48 + (0.5 + nas9) kas49) + (0.5 + nas5) ^2 kas55 +
  (0.5 + nas5) ((0.5 + nas6) kas56 + (0.5 + nas7) kas57 + (0.5 + nas8) kas58 + (0.5 + nas9) kas59) +
  (0.5 + nas6) ^2 kas66 +
  (0.5 + nas6) ((0.5 + nas7) kas67 + (0.5 + nas8) kas68 + (0.5 + nas9) kas69) +
  (0.5 + nas7) ^2 kas77 + (0.5 + nas7) ((0.5 + nas8) kas78 + (0.5 + nas9) kas79) +
  (0.5 + nas8) ^2 kas88 + (0.5 + nas8) (0.5 + nas9) kas89 + (0.5 + nas9) ^2 kas99

n1 = n2 = n3 = n4 = n5 = n6 = nas4 = nas5 = nas6 = nas7 = nas8 = nas9 = 14 = 15 = 16 = 0

0

w7 = w4

w4

```

Figure A.7: Determination of the difference between the zero point energies (ZPE) continued.

 $dE.nb$

3

```

w8 = w5

w5

w9 = w6

w6

Variables[Easym - Esym]

{w1, w2, w3, w4, w5, w6, k11, k12, k13, k14, k15, k16, k22, k23, k24, k25, k26, k33, k34,
 k35, k36, k44, k45, k46, k55, k56, k66, kas14, kas15, kas16, kas17, kas18, kas19,
 kas24, kas25, kas26, kas27, kas28, kas29, kas34, kas35, kas36, kas37, kas38,
 kas39, kas44, kas45, kas46, kas47, kas48, kas49, kas55, kas56, kas57, kas58,
 kas59, kas66, kas67, kas68, kas69, kas77, kas78, kas79, kas88, kas89, kas99}

E0asym = Easym

0.5w1 + 0.5w2 + 0.5w3 + 1. w4 + 1. w5 + 1. w6 + 0.25k11 + 0.25k12 + 0.25k13 + 0.25k22 + 0.25k23 +
0.25k33 + 0.5 (0.5kas14 + 0.5kas15 + 0.5kas16 + 0.5kas17 + 0.5kas18 + 0.5kas19) +
0.5 (0.5kas24 + 0.5kas25 + 0.5kas26 + 0.5kas27 + 0.5kas28 + 0.5kas29) +
0.5 (0.5kas34 + 0.5kas35 + 0.5kas36 + 0.5kas37 + 0.5kas38 + 0.5kas39) +
0.25kas44 + 0.5 (0.5kas45 + 0.5kas46 + 0.5kas47 + 0.5kas48 + 0.5kas49) +
0.25kas55 + 0.5 (0.5kas56 + 0.5kas57 + 0.5kas58 + 0.5kas59) +
0.25kas66 + 0.5 (0.5kas67 + 0.5kas68 + 0.5kas69) + 0.25kas77 +
0.5 (0.5kas78 + 0.5kas79) + 0.25kas88 + 0.25kas89 + 0.25kas99

E0sym = Esym

0.5w1 + 0.5w2 + 0.5w3 + w4 + w5 + w6 + 0.25k11 + 0.25k12 +
0.25k13 + 0.5 (k14 + k15 + k16) + 0.25k22 + 0.25k23 + 0.5 (k24 + k25 + k26) +
0.25k33 + 0.5 (k34 + k35 + k36) + k44 + k45 + k46 + k55 + k56 + k66

dE = E0sym - E0asym

0. w1 + 0. w2 + 0. w3 + 0. w4 + 0. w5 + 0. w6 + 0. k11 + 0. k12 + 0. k13 + 0.5 (k14 + k15 + k16) +
0. k22 + 0. k23 + 0.5 (k24 + k25 + k26) + 0. k33 + 0.5 (k34 + k35 + k36) + k44 + k45 + k46 + k55 +
k56 + k66 - 0.5 (0.5kas14 + 0.5kas15 + 0.5kas16 + 0.5kas17 + 0.5kas18 + 0.5kas19) -
0.5 (0.5kas24 + 0.5kas25 + 0.5kas26 + 0.5kas27 + 0.5kas28 + 0.5kas29) -
0.5 (0.5kas34 + 0.5kas35 + 0.5kas36 + 0.5kas37 + 0.5kas38 + 0.5kas39) -
0.25kas44 - 0.5 (0.5kas45 + 0.5kas46 + 0.5kas47 + 0.5kas48 + 0.5kas49) -
0.25kas55 - 0.5 (0.5kas56 + 0.5kas57 + 0.5kas58 + 0.5kas59) -
0.25kas66 - 0.5 (0.5kas67 + 0.5kas68 + 0.5kas69) - 0.25kas77 -
0.5 (0.5kas78 + 0.5kas79) - 0.25kas88 - 0.25kas89 - 0.25kas99

```

2. Determination of g_{66} for $n_6 = l_6 = 1$ and $nas_6 = 1$, $nas_9 = 0$..

Figure A.8: Determination of g_{66} .*g66.nb*

1

```

omsym = w1 (n1 + 0.5) + w2 (n2 + 0.5) + w3 (n3 + 0.5) + w4 (n4 + 1) + w5 (n5 + 1) + w6 (n6 + 1)

(0.5 + n1) w1 + (0.5 + n2) w2 + (0.5 + n3) w3 + (1 + n4) w4 + (1 + n5) w5 + (1 + n6) w6

xsssym = x11 (n1 + 0.5) ^2 + x22 (n2 + 0.5) ^2 + x33 (n3 + 0.5) ^2 +
  x12 (n1 + 0.5) (n2 + 0.5) + x13 (n1 + 0.5) (n3 + 0.5) + x23 (n2 + 0.5) (n3 + 0.5)

(0.5 + n1) ^2 x11 + (0.5 + n1) (0.5 + n2) x12 + (0.5 + n1) (0.5 + n3) x13 +
  (0.5 + n2) ^2 x22 + (0.5 + n2) (0.5 + n3) x23 + (0.5 + n3) ^2 x33

xstsym = (n1 + 0.5) (x14 (n4 + 1) + x15 (n5 + 1) + x16 (n6 + 1)) +
  (n2 + 0.5) (x24 (n4 + 1) + x25 (n5 + 1) + x26 (n6 + 1)) +
  (n3 + 0.5) (x34 (n4 + 1) + x35 (n5 + 1) + x36 (n6 + 1))

General::spell11: Possible spelling error: new symbol name "xstsym" is similar to existing symbol "xsssym".

(0.5 + n1) ((1 + n4) x14 + (1 + n5) x15 + (1 + n6) x16) +
  (0.5 + n2) ((1 + n4) x24 + (1 + n5) x25 + (1 + n6) x26) +
  (0.5 + n3) ((1 + n4) x34 + (1 + n5) x35 + (1 + n6) x36)

xttsym = x44 (n4 + 1) ^2 + x55 (n5 + 1) ^2 + x66 (n6 + 1) ^2 +
  x45 (n4 + 1) (n5 + 1) + x46 (n4 + 1) (n6 + 1) + x56 (n5 + 1) (n6 + 1)

General::spell11: Possible spelling error: new symbol name "xttsym" is similar to existing symbol "xstsym".

(1 + n4) ^2 x44 + (1 + n4) (1 + n5) x45 + (1 + n4) (1 + n6) x46 +
  (1 + n5) ^2 x55 + (1 + n5) (1 + n6) x56 + (1 + n6) ^2 x66

gttsym = g44 * 14 ^2 + g55 * 15 ^2 + g66 * 16 ^2 + g45 * 14 * 15 + g46 * 14 * 16 + g56 * 15 * 16

General::spell11: Possible spelling error: new symbol name "gttsym" is similar to existing symbol "xttsym".

g44 14^2 + g45 14 15 + g55 15^2 + g46 14 16 + g56 15 16 + g66 16^2

Esym = omsym + xsssym + xstsym + xttsym + gttsym

g44 14^2 + g45 14 15 + g55 15^2 + g46 14 16 + g56 15 16 + g66 16^2 + (0.5 + n1) w1 +
  (0.5 + n2) w2 + (0.5 + n3) w3 + (1 + n4) w4 + (1 + n5) w5 + (1 + n6) w6 +
  (0.5 + n1) ^2 x11 + (0.5 + n1) (0.5 + n2) x12 + (0.5 + n1) (0.5 + n3) x13 +
  (0.5 + n1) ((1 + n4) x14 + (1 + n5) x15 + (1 + n6) x16) + (0.5 + n2) ^2 x22 +
  (0.5 + n2) (0.5 + n3) x23 + (0.5 + n2) ((1 + n4) x24 + (1 + n5) x25 + (1 + n6) x26) +
  (0.5 + n3) ^2 x33 + (0.5 + n3) ((1 + n4) x34 + (1 + n5) x35 + (1 + n6) x36) + (1 + n4) ^2 x44 +
  (1 + n4) (1 + n5) x45 + (1 + n4) (1 + n6) x46 + (1 + n5) ^2 x55 + (1 + n5) (1 + n6) x56 + (1 + n6) ^2 x66

omasym = w1 (n1 + 0.5) + w2 (n2 + 0.5) + w3 (n3 + 0.5) + w4 (nas4 + 0.5) +
  w5 (nas5 + 0.5) + w6 (nas6 + 0.5) + w7 (nas7 + 0.5) + w8 (nas8 + 0.5) + w9 (nas9 + 0.5)

General::spell11: Possible spelling error: new symbol name "omasym" is similar to existing symbol "omsym".

(0.5 + n1) w1 + (0.5 + n2) w2 + (0.5 + n3) w3 + (0.5 + nas4) w4 +
  (0.5 + nas5) w5 + (0.5 + nas6) w6 + (0.5 + nas7) w7 + (0.5 + nas8) w8 + (0.5 + nas9) w9

xssasym = x11 (n1 + 0.5) ^2 + x22 (n2 + 0.5) ^2 + x33 (n3 + 0.5) ^2 +
  x12 (n1 + 0.5) (n2 + 0.5) + x23 (n2 + 0.5) (n3 + 0.5) + x13 (n1 + 0.5) (n3 + 0.5)

General::spell11: Possible spelling error: new symbol name "xssasym" is similar to existing symbol "xsssym".

(0.5 + n1) ^2 x11 + (0.5 + n1) (0.5 + n2) x12 + (0.5 + n1) (0.5 + n3) x13 +
  (0.5 + n2) ^2 x22 + (0.5 + n2) (0.5 + n3) x23 + (0.5 + n3) ^2 x33

```

Figure A.9: Determination of g_{66} continued. $g_{66}.nb$

2

```

xstasym = (n1+0.5) (kas14 (nas4+0.5) + kas15 (nas5+0.5) +
  kas16 (nas6+0.5) + kas17 (nas7+0.5) + kas18 (nas8+0.5) + kas19 (nas9+0.5) ) +
  (n2+0.5) (kas24 (nas4+0.5) + kas25 (nas5+0.5) + kas26 (nas6+0.5) +
  kas27 (nas7+0.5) + kas28 (nas8+0.5) + kas29 (nas9+0.5) ) +
  (n3+0.5) (kas34 (nas4+0.5) + kas35 (nas5+0.5) + kas36 (nas6+0.5) +
  kas37 (nas7+0.5) + kas38 (nas8+0.5) + kas39 (nas9+0.5) )

General::spell :
Possible spelling error: new symbol name "xstasym" is similar to existing symbols {xmasym, xtasym}.

(0.5+n1) ((0.5+nas4) kas14 + (0.5+nas5) kas15 +
  (0.5+nas6) kas16 + (0.5+nas7) kas17 + (0.5+nas8) kas18 + (0.5+nas9) kas19) +
(0.5+n2) ((0.5+nas4) kas24 + (0.5+nas5) kas25 + (0.5+nas6) kas26 +
  (0.5+nas7) kas27 + (0.5+nas8) kas28 + (0.5+nas9) kas29) +
(0.5+n3) ((0.5+nas4) kas34 + (0.5+nas5) kas35 + (0.5+nas6) kas36 +
  (0.5+nas7) kas37 + (0.5+nas8) kas38 + (0.5+nas9) kas39)

xttasym = kas44 (nas4+0.5)^2 + kas55 (nas5+0.5)^2 +
  kas66 (nas6+0.5)^2 + kas77 (nas7+0.5)^2 + kas88 (nas8+0.5)^2 +
  kas99 (nas9+0.5)^2 + (nas4+0.5) (kas45 (nas5+0.5) + kas46 (nas6+0.5) +
  kas47 (nas7+0.5) + kas48 (nas8+0.5) + kas49 (nas9+0.5) ) + (nas5+0.5)
  (kas56 (nas6+0.5) + kas57 (nas7+0.5) + kas58 (nas8+0.5) + kas59 (nas9+0.5) ) +
  (nas6+0.5) (kas67 (nas7+0.5) + kas68 (nas8+0.5) + kas69 (nas9+0.5) ) +
  (nas7+0.5) (kas78 (nas8+0.5) + kas79 (nas9+0.5) ) + kas89 (nas8+0.5) (nas9+0.5)

General::spell :
Possible spelling error: new symbol name "xttasym" is similar to existing symbols {xstasym, xtasym}.

(0.5+nas4)^2 kas44 +
(0.5+nas4) ((0.5+nas5) kas45 + (0.5+nas6) kas46 + (0.5+nas7) kas47 + (0.5+nas8) kas48 +
  (0.5+nas9) kas49) + (0.5+nas5)^2 kas55 + (0.5+nas5)
  ((0.5+nas6) kas56 + (0.5+nas7) kas57 + (0.5+nas8) kas58 + (0.5+nas9) kas59) +
(0.5+nas6)^2 kas66 + (0.5+nas6)
  ((0.5+nas7) kas67 + (0.5+nas8) kas68 + (0.5+nas9) kas69) +
(0.5+nas7)^2 kas77 + (0.5+nas7) ((0.5+nas8) kas78 + (0.5+nas9) kas79) +
(0.5+nas8)^2 kas88 + (0.5+nas8) (0.5+nas9) kas89 + (0.5+nas9)^2 kas99

Easym = omasym + xssasym + xstasym + xttasym

General::spell1 : Possible spelling error: new symbol name "Easym" is similar to existing symbol "Esym".

(0.5+n1) w1 + (0.5+n2) w2 + (0.5+n3) w3 + (0.5+nas4) w4 + (0.5+nas5) w5 +
  (0.5+nas6) w6 + (0.5+nas7) w7 + (0.5+nas8) w8 + (0.5+nas9) w9 + (0.5+n1)^2 x11 +
  (0.5+n1) (0.5+n2) x12 + (0.5+n1) (0.5+n3) x13 + (0.5+n2)^2 x22 +
  (0.5+n2) (0.5+n3) x23 + (0.5+n3)^2 x33 + (0.5+n1) ((0.5+nas4) kas14 + (0.5+nas5) kas15 +
  (0.5+nas6) kas16 + (0.5+nas7) kas17 + (0.5+nas8) kas18 + (0.5+nas9) kas19) +
  (0.5+n2) ((0.5+nas4) kas24 + (0.5+nas5) kas25 + (0.5+nas6) kas26 +
  (0.5+nas7) kas27 + (0.5+nas8) kas28 + (0.5+nas9) kas29) +
  (0.5+n3) ((0.5+nas4) kas34 + (0.5+nas5) kas35 + (0.5+nas6) kas36 +
  (0.5+nas7) kas37 + (0.5+nas8) kas38 + (0.5+nas9) kas39) + (0.5+nas4)^2 kas44 +
  (0.5+nas4) ((0.5+nas5) kas45 + (0.5+nas6) kas46 + (0.5+nas7) kas47 +
  (0.5+nas8) kas48 + (0.5+nas9) kas49) + (0.5+nas5)^2 kas55 + (0.5+nas5)
  ((0.5+nas6) kas56 + (0.5+nas7) kas57 + (0.5+nas8) kas58 + (0.5+nas9) kas59) +
  (0.5+nas6)^2 kas66 + (0.5+nas6)
  ((0.5+nas7) kas67 + (0.5+nas8) kas68 + (0.5+nas9) kas69) +
  (0.5+nas7)^2 kas77 + (0.5+nas7) ((0.5+nas8) kas78 + (0.5+nas9) kas79) +
  (0.5+nas8)^2 kas88 + (0.5+nas8) (0.5+nas9) kas89 + (0.5+nas9)^2 kas99

w7 = w4

w4

w8 = w5

w5

```

Figure A.10: Determination of g_{66} continued.*g66.nb*

3

```

w9 = w6

w6

de = 0.5` (x14 + x15 + x16) + 0.5` (x24 + x25 + x26) + 0.5` (x34 + x35 + x36) + x44 + x45 + x46 + x55 +
x56 + x66 - 0.5` (0.5` kas14 + 0.5` kas15 + 0.5` kas16 + 0.5` kas17 + 0.5` kas18 + 0.5` kas19) -
0.5` (0.5` kas24 + 0.5` kas25 + 0.5` kas26 + 0.5` kas27 + 0.5` kas28 + 0.5` kas29) -
0.5` (0.5` kas34 + 0.5` kas35 + 0.5` kas36 + 0.5` kas37 + 0.5` kas38 + 0.5` kas39) -
0.25` kas44 - 0.5` (0.5` kas45 + 0.5` kas46 + 0.5` kas47 + 0.5` kas48 + 0.5` kas49) -
0.25` kas55 - 0.5` (0.5` kas56 + 0.5` kas57 + 0.5` kas58 + 0.5` kas59) -
0.25` kas66 - 0.5` (0.5` kas67 + 0.5` kas68 + 0.5` kas69) - 0.25` kas77 -
0.5` (0.5` kas78 + 0.5` kas79) - 0.25` kas88 - 0.25` kas89 - 0.25` kas99

0.5` (x14 + x15 + x16) + 0.5` (x24 + x25 + x26) + 0.5` (x34 + x35 + x36) + x44 + x45 + x46 + x55 +
x56 + x66 - 0.5` (0.5` kas14 + 0.5` kas15 + 0.5` kas16 + 0.5` kas17 + 0.5` kas18 + 0.5` kas19) -
0.5` (0.5` kas24 + 0.5` kas25 + 0.5` kas26 + 0.5` kas27 + 0.5` kas28 + 0.5` kas29) -
0.5` (0.5` kas34 + 0.5` kas35 + 0.5` kas36 + 0.5` kas37 + 0.5` kas38 + 0.5` kas39) -
0.25` kas44 - 0.5` (0.5` kas45 + 0.5` kas46 + 0.5` kas47 + 0.5` kas48 + 0.5` kas49) -
0.25` kas55 - 0.5` (0.5` kas56 + 0.5` kas57 + 0.5` kas58 + 0.5` kas59) -
0.25` kas66 - 0.5` (0.5` kas67 + 0.5` kas68 + 0.5` kas69) - 0.25` kas77 -
0.5` (0.5` kas78 + 0.5` kas79) - 0.25` kas88 - 0.25` kas89 - 0.25` kas99

n1 = n2 = n3 = n4 = n5 = nas4 = nas5 = nas7 = nas8 = 14 = 15 = 0

0

n6 = 16 = 1

1

nas6 = 1

1

nas9 = 0

0

kas17 = kas14

kas14

x14 = 0.5` (kas14 + kas17)

1. kas14

kas18 = kas15

kas15

x15 = 0.5` (kas15 + kas18)

1. kas15

kas19 = kas16

kas16

```

Figure A.11: Determination of g_{66} continued.*g66.nb*

4

```

x16 = 0.5 (xas16 + xas19)
1. xas16

xas27 = xas24
xas24

x24 = 0.5 (xas24 + xas27)
1. xas24

xas28 = xas25
xas25

x25 = 0.5 (xas25 + xas28)
1. xas25

xas29 = xas26
xas26

x26 = 0.5 (xas26 + xas29)
1. xas26

xas37 = xas34
xas34

x34 = 0.5 (xas34 + xas37)
1. xas34

xas38 = xas35
xas35

x35 = 0.5 (xas35 + xas38)
1. xas35

xas39 = xas36
xas36

x36 = 0.5 (xas36 + xas39)
1. xas36

xas77 = xas44
xas44

```

Figure A.12: Determination of g_{66} continued.*g66.nb*

5

```

kas88 = kas55

kas55

kas99 = kas66

kas66

kas78 = kas45

kas45

kas79 = kas46

kas46

kas89 = kas56

kas56

kas67 = kas49

kas49

kas68 = kas59

kas59

kas57 = kas48

kas48

dde = Easym - Esym + dE

-g66 + 0. w1 + 0. w2 + 0. w3 + 0. w4 + 0. w5 + 0. w6 + 0. x11 + 0. x12 + 0. x13 +
0. x22 + 0. x23 + 0. x33 - x46 - x56 - 3 x66 + 0. (1. kas14 + 1. kas15 + 1. kas16) +
0. (1. kas14 + 1. kas15 + 2. kas16) + 0. (1. kas24 + 1. kas25 + 1. kas26) +
0. (1. kas24 + 1. kas25 + 2. kas26) + 0. (1. kas34 + 1. kas35 + 1. kas36) +
0. (1. kas34 + 1. kas35 + 2. kas36) + 0. kas44 + 0. (0.5 kas45 + 0.5 kas46) -
0.5 (0.5 kas45 + 0.5 kas46 + 0.5 kas47 + 0.5 kas48 + 0.5 kas49) +
0.5 (0.5 kas45 + 1.5 kas46 + 0.5 kas47 + 0.5 kas48 + 0.5 kas49) +
0. kas55 + 0. kas56 - 0.5 (0.5 kas48 + 0.5 kas56 + 0.5 kas58 + 0.5 kas59) +
0.5 (0.5 kas48 + 1.5 kas56 + 0.5 kas58 + 0.5 kas59) +
2. kas66 + 1. (0.5 kas49 + 0.5 kas59 + 0.5 kas69)

Simplify[dde]

-g66 + 0. w1 + 0. w2 + 0. w3 + 0. w4 + 0. w5 + 0. w6 + 0. x11 + 0. x12 + 0. x13 + 0. x22 +
0. x23 + 0. x33 - x46 - x56 - 3 x66 + 0. kas14 + 0. kas15 + 0. kas16 + 0. kas24 + 0. kas25 +
0. kas26 + 0. kas34 + 0. kas35 + 0. kas36 + 0. kas44 + 0. kas45 + 0.5 kas46 + 0. kas47 +
0. kas48 + 0.5 kas49 + 0. kas55 + 0.5 kas56 + 0. kas58 + 0.5 kas59 + 2. kas66 + 0.5 kas69

Simplify[Solve[dde == 0]]

Solve::vars : Equations may not give solutions for all "solve" variables.

{{g66 == 0. -1. x46 - 1. x56 - 3. x66 +
0.5 kas46 + 0.5 kas49 + 0.5 kas56 + 0.5 kas59 + 2. kas66 + 0.5 kas69}}
```

3. Determination of x_{46} for $n_6 = l_6 = 2$ and $nas_6 = nas_9 = 1$.

Figure A.13: Determination of x_{46} . $x_{46}.nb$

1

```

omsym = w1 (n1 + 0.5) + w2 (n2 + 0.5) + w3 (n3 + 0.5) + w4 (n4 + 1) + w5 (n5 + 1) + w6 (n6 + 1)

(0.5 + n1) w1 + (0.5 + n2) w2 + (0.5 + n3) w3 + (1 + n4) w4 + (1 + n5) w5 + (1 + n6) w6

xsssym = x11 (n1 + 0.5) ^2 + x22 (n2 + 0.5) ^2 + x33 (n3 + 0.5) ^2 +
  x12 (n1 + 0.5) (n2 + 0.5) + x13 (n1 + 0.5) (n3 + 0.5) + x23 (n2 + 0.5) (n3 + 0.5)

(0.5 + n1) ^2 x11 + (0.5 + n1) (0.5 + n2) x12 + (0.5 + n1) (0.5 + n3) x13 +
(0.5 + n2) ^2 x22 + (0.5 + n2) (0.5 + n3) x23 + (0.5 + n3) ^2 x33

xstsym = (n1 + 0.5) (x14 (n4 + 1) + x15 (n5 + 1) + x16 (n6 + 1)) +
  (n2 + 0.5) (x24 (n4 + 1) + x25 (n5 + 1) + x26 (n6 + 1)) +
  (n3 + 0.5) (x34 (n4 + 1) + x35 (n5 + 1) + x36 (n6 + 1))

General::spell11 : Possible spelling error: new symbol name "xstsym" is similar to existing symbol "xsssym".

(0.5 + n1) ((1 + n4) x14 + (1 + n5) x15 + (1 + n6) x16) +
(0.5 + n2) ((1 + n4) x24 + (1 + n5) x25 + (1 + n6) x26) +
(0.5 + n3) ((1 + n4) x34 + (1 + n5) x35 + (1 + n6) x36)

xttsym = x44 (n4 + 1) ^2 + x55 (n5 + 1) ^2 + x66 (n6 + 1) ^2 +
  x45 (n4 + 1) (n5 + 1) + x46 (n4 + 1) (n6 + 1) + x56 (n5 + 1) (n6 + 1)

General::spell11 : Possible spelling error: new symbol name "xttsym" is similar to existing symbol "xstsym".

(1 + n4) ^2 x44 + (1 + n4) (1 + n5) x45 + (1 + n4) (1 + n6) x46 +
(1 + n5) ^2 x55 + (1 + n5) (1 + n6) x56 + (1 + n6) ^2 x66

gttsym = g44 * 14 ^2 + g55 * 15 ^2 + g66 * 16 ^2 + g45 * 14 * 15 + g46 * 14 * 16 + g56 * 15 * 16

General::spell11 : Possible spelling error: new symbol name "gttsym" is similar to existing symbol "xttsym".

g44 14^2 + g45 14 15 + g55 15^2 + g46 14 16 + g56 15 16 + g66 16^2

Esym = omsym + xsssym + xstsym + xttsym + gttsym

g44 14^2 + g45 14 15 + g55 15^2 + g46 14 16 + g56 15 16 + g66 16^2 + (0.5 + n1) w1 +
(0.5 + n2) w2 + (0.5 + n3) w3 + (1 + n4) w4 + (1 + n5) w5 + (1 + n6) w6 +
(0.5 + n1) ^2 x11 + (0.5 + n1) (0.5 + n2) x12 + (0.5 + n1) (0.5 + n3) x13 +
(0.5 + n1) ((1 + n4) x14 + (1 + n5) x15 + (1 + n6) x16) + (0.5 + n2) ^2 x22 +
(0.5 + n2) (0.5 + n3) x23 + (0.5 + n2) ((1 + n4) x24 + (1 + n5) x25 + (1 + n6) x26) +
(0.5 + n3) ^2 x33 + (0.5 + n3) ((1 + n4) x34 + (1 + n5) x35 + (1 + n6) x36) + (1 + n4) ^2 x44 +
(1 + n4) (1 + n5) x45 + (1 + n4) (1 + n6) x46 + (1 + n5) ^2 x55 + (1 + n5) (1 + n6) x56 + (1 + n6) ^2 x66

omasym = w1 (n1 + 0.5) + w2 (n2 + 0.5) + w3 (n3 + 0.5) + w4 (nas4 + 0.5) +
  w5 (nas5 + 0.5) + w6 (nas6 + 0.5) + w7 (nas7 + 0.5) + w8 (nas8 + 0.5) + w9 (nas9 + 0.5)

General::spell11 : Possible spelling error: new symbol name "omasym" is similar to existing symbol "omsym".

(0.5 + n1) w1 + (0.5 + n2) w2 + (0.5 + n3) w3 + (0.5 + nas4) w4 +
(0.5 + nas5) w5 + (0.5 + nas6) w6 + (0.5 + nas7) w7 + (0.5 + nas8) w8 + (0.5 + nas9) w9

xssasym = x11 (n1 + 0.5) ^2 + x22 (n2 + 0.5) ^2 + x33 (n3 + 0.5) ^2 +
  x12 (n1 + 0.5) (n2 + 0.5) + x23 (n2 + 0.5) (n3 + 0.5) + x13 (n1 + 0.5) (n3 + 0.5)

General::spell11 : Possible spelling error: new symbol name "xssasym" is similar to existing symbol "xsssym".

(0.5 + n1) ^2 x11 + (0.5 + n1) (0.5 + n2) x12 + (0.5 + n1) (0.5 + n3) x13 +
(0.5 + n2) ^2 x22 + (0.5 + n2) (0.5 + n3) x23 + (0.5 + n3) ^2 x33

```

Figure A.14: Determination of $x46$ continued. $x46.nb$

2

```

xstasym = (n1 + 0.5) (kas14 (nas4 + 0.5) + kas15 (nas5 + 0.5) +
  kas16 (nas6 + 0.5) + kas17 (nas7 + 0.5) + kas18 (nas8 + 0.5) + kas19 (nas9 + 0.5) ) +
  (n2 + 0.5) (kas24 (nas4 + 0.5) + kas25 (nas5 + 0.5) + kas26 (nas6 + 0.5) +
  kas27 (nas7 + 0.5) + kas28 (nas8 + 0.5) + kas29 (nas9 + 0.5) ) +
  (n3 + 0.5) (kas34 (nas4 + 0.5) + kas35 (nas5 + 0.5) + kas36 (nas6 + 0.5) +
  kas37 (nas7 + 0.5) + kas38 (nas8 + 0.5) + kas39 (nas9 + 0.5) )

General::spell :
Possible spelling error: new symbol name "xstasym" is similar to existing symbols {xmasym, xtasym}.

(0.5 + n1) ((0.5 + nas4) kas14 + (0.5 + nas5) kas15 +
  (0.5 + nas6) kas16 + (0.5 + nas7) kas17 + (0.5 + nas8) kas18 + (0.5 + nas9) kas19) +
(0.5 + n2) ((0.5 + nas4) kas24 + (0.5 + nas5) kas25 + (0.5 + nas6) kas26 +
  (0.5 + nas7) kas27 + (0.5 + nas8) kas28 + (0.5 + nas9) kas29) +
(0.5 + n3) ((0.5 + nas4) kas34 + (0.5 + nas5) kas35 + (0.5 + nas6) kas36 +
  (0.5 + nas7) kas37 + (0.5 + nas8) kas38 + (0.5 + nas9) kas39)

xttasym = kas44 (nas4 + 0.5) ^2 + kas55 (nas5 + 0.5) ^2 +
  kas66 (nas6 + 0.5) ^2 + kas77 (nas7 + 0.5) ^2 + kas88 (nas8 + 0.5) ^2 +
  kas99 (nas9 + 0.5) ^2 + (nas4 + 0.5) (kas45 (nas5 + 0.5) + kas46 (nas6 + 0.5) +
  kas47 (nas7 + 0.5) + kas48 (nas8 + 0.5) + kas49 (nas9 + 0.5) ) + (nas5 + 0.5)
  (kas56 (nas6 + 0.5) + kas57 (nas7 + 0.5) + kas58 (nas8 + 0.5) + kas59 (nas9 + 0.5) ) +
  (nas6 + 0.5) (kas67 (nas7 + 0.5) + kas68 (nas8 + 0.5) + kas69 (nas9 + 0.5) ) +
  (nas7 + 0.5) (kas78 (nas8 + 0.5) + kas79 (nas9 + 0.5) ) + kas89 (nas8 + 0.5) (nas9 + 0.5)

General::spell :
Possible spelling error: new symbol name "xttasym" is similar to existing symbols {xstasym, xtasym}.

(0.5 + nas4) ^2 kas44 +
(0.5 + nas4) ((0.5 + nas5) kas45 + (0.5 + nas6) kas46 + (0.5 + nas7) kas47 + (0.5 + nas8) kas48 +
  (0.5 + nas9) kas49) + (0.5 + nas5) ^2 kas55 + (0.5 + nas5)
  ((0.5 + nas6) kas56 + (0.5 + nas7) kas57 + (0.5 + nas8) kas58 + (0.5 + nas9) kas59) +
(0.5 + nas6) ^2 kas66 + (0.5 + nas6)
  ((0.5 + nas7) kas67 + (0.5 + nas8) kas68 + (0.5 + nas9) kas69) +
(0.5 + nas7) ^2 kas77 + (0.5 + nas7) ((0.5 + nas8) kas78 + (0.5 + nas9) kas79) +
(0.5 + nas8) ^2 kas88 + (0.5 + nas8) (0.5 + nas9) kas89 + (0.5 + nas9) ^2 kas99

Easym = omasym + xssasym + xstasym + xttasym

General::spell1 : Possible spelling error: new symbol name "Easym" is similar to existing symbol "Esym".

(0.5 + n1) w1 + (0.5 + n2) w2 + (0.5 + n3) w3 + (0.5 + nas4) w4 + (0.5 + nas5) w5 +
  (0.5 + nas6) w6 + (0.5 + nas7) w7 + (0.5 + nas8) w8 + (0.5 + nas9) w9 + (0.5 + n1) ^2 x11 +
  (0.5 + n1) (0.5 + n2) x12 + (0.5 + n1) (0.5 + n3) x13 + (0.5 + n2) ^2 x22 +
  (0.5 + n2) (0.5 + n3) x23 + (0.5 + n3) ^2 x33 + (0.5 + n1) ((0.5 + nas4) kas14 + (0.5 + nas5) kas15 +
  (0.5 + nas6) kas16 + (0.5 + nas7) kas17 + (0.5 + nas8) kas18 + (0.5 + nas9) kas19) +
  (0.5 + n2) ((0.5 + nas4) kas24 + (0.5 + nas5) kas25 + (0.5 + nas6) kas26 +
  (0.5 + nas7) kas27 + (0.5 + nas8) kas28 + (0.5 + nas9) kas29) +
  (0.5 + n3) ((0.5 + nas4) kas34 + (0.5 + nas5) kas35 + (0.5 + nas6) kas36 +
  (0.5 + nas7) kas37 + (0.5 + nas8) kas38 + (0.5 + nas9) kas39) + (0.5 + nas4) ^2 kas44 +
  (0.5 + nas4) ((0.5 + nas5) kas45 + (0.5 + nas6) kas46 + (0.5 + nas7) kas47 +
  (0.5 + nas8) kas48 + (0.5 + nas9) kas49) + (0.5 + nas5) ^2 kas55 + (0.5 + nas5)
  ((0.5 + nas6) kas56 + (0.5 + nas7) kas57 + (0.5 + nas8) kas58 + (0.5 + nas9) kas59) +
  (0.5 + nas6) ^2 kas66 + (0.5 + nas6)
  ((0.5 + nas7) kas67 + (0.5 + nas8) kas68 + (0.5 + nas9) kas69) +
  (0.5 + nas7) ^2 kas77 + (0.5 + nas7) ((0.5 + nas8) kas78 + (0.5 + nas9) kas79) +
  (0.5 + nas8) ^2 kas88 + (0.5 + nas8) (0.5 + nas9) kas89 + (0.5 + nas9) ^2 kas99

w7 = w4

w4

w8 = w5

w5

```

Figure A.15: Determination of x_{46} continued. $x_{46}.nb$

3

```

w9 = w6

w6

dB = 0.5 * (x14 + x15 + x16) + 0.5 * (x24 + x25 + x26) + 0.5 * (x34 + x35 + x36) + x44 + x45 + x46 + x55 +
x56 + x66 - 0.5 * (0.5 * kas14 + 0.5 * kas15 + 0.5 * kas16 + 0.5 * kas17 + 0.5 * kas18 + 0.5 * kas19) -
0.5 * (0.5 * kas24 + 0.5 * kas25 + 0.5 * kas26 + 0.5 * kas27 + 0.5 * kas28 + 0.5 * kas29) -
0.5 * (0.5 * kas34 + 0.5 * kas35 + 0.5 * kas36 + 0.5 * kas37 + 0.5 * kas38 + 0.5 * kas39) -
0.25 * kas44 - 0.5 * (0.5 * kas45 + 0.5 * kas46 + 0.5 * kas47 + 0.5 * kas48 + 0.5 * kas49) -
0.25 * kas55 - 0.5 * (0.5 * kas56 + 0.5 * kas57 + 0.5 * kas58 + 0.5 * kas59) -
0.25 * kas66 - 0.5 * (0.5 * kas67 + 0.5 * kas68 + 0.5 * kas69) - 0.25 * kas77 -
0.5 * (0.5 * kas78 + 0.5 * kas79) - 0.25 * kas88 - 0.25 * kas89 - 0.25 * kas99

0.5 * (x14 + x15 + x16) + 0.5 * (x24 + x25 + x26) + 0.5 * (x34 + x35 + x36) + x44 + x45 + x46 + x55 +
x56 + x66 - 0.5 * (0.5 * kas14 + 0.5 * kas15 + 0.5 * kas16 + 0.5 * kas17 + 0.5 * kas18 + 0.5 * kas19) -
0.5 * (0.5 * kas24 + 0.5 * kas25 + 0.5 * kas26 + 0.5 * kas27 + 0.5 * kas28 + 0.5 * kas29) -
0.5 * (0.5 * kas34 + 0.5 * kas35 + 0.5 * kas36 + 0.5 * kas37 + 0.5 * kas38 + 0.5 * kas39) -
0.25 * kas44 - 0.5 * (0.5 * kas45 + 0.5 * kas46 + 0.5 * kas47 + 0.5 * kas48 + 0.5 * kas49) -
0.25 * kas55 - 0.5 * (0.5 * kas56 + 0.5 * kas57 + 0.5 * kas58 + 0.5 * kas59) -
0.25 * kas66 - 0.5 * (0.5 * kas67 + 0.5 * kas68 + 0.5 * kas69) - 0.25 * kas77 -
0.5 * (0.5 * kas78 + 0.5 * kas79) - 0.25 * kas88 - 0.25 * kas89 - 0.25 * kas99

n1 = n2 = n3 = n4 = n5 = nas4 = nas5 = nas7 = nas8 = 14 = 15 = 0

0

n6 = 16 = 2

2

nas6 = 1

1

nas9 = 1

1

kas17 = kas14

kas14

x14 = 0.5 * (kas14 + kas17)

1. kas14

kas18 = kas15

kas15

x15 = 0.5 * (kas15 + kas18)

1. kas15

kas19 = kas16

kas16

```